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DENSITIES AND MELTING POINTS
OF
NORMAL STRAIGHT-CHAIN HYDROCARBONS

by

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PREFACE

The work described in this thesis represents: (1) the author's own researches during the past year, and (2) a correlation of this work with that of other workers in the same field, particularly of those who preceded the author in this laboratory.

The ultimate purpose of this project was to collect data on the normal straight-chain hydrocarbons, such data to be of value to the petroleum industry and those working with petroleum products. That the petroleum industry is interested in such information is proved by the fact that it sponsors a vast amount of physical and chemical research. In particular, the present work was made possible by a scholarship from the Standard Oil Company of British Columbia, and the author wishes to express his thanks for this assistance.

In addition, the author would like to thank Dr. W.F. Seyer, of the Department of Chemistry, for his constant help and advice throughout the course of the work.

Several of the senior students, also, gave valuable assistance in the preparation and purification of the hydrocarbons; two of the most helpful were E.L. Smith, and S. Cavers.

Signed:

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DENSITIES AND MELTING POINTS OF NORMAL STRAIGHT-CHAIN HYDROCARBONS

This investigation and others carried out in the same laboratory are intended to serve two ends. From a purely theoretical point of view, they add to the general accumulation of scientific data. In addition, they are a primary need in design work. The design of plants or the development of chemical processes on a commercial scale will be, in general, efficient and profitable in direct proportion to the number of unknown factors which can be eliminated. These unknowns usually involve physical constants of the reacting substances.

The precipitation of the heavy hydrocarbons in petroleum by the addition of light paraffins may be taken as a practical example of the need for exact physical data. In order to increase the efficiency of the process, it was first necessary to obtain accurate and complete data on the mutual solubility of the paraffins. A study of these solubilities led to an investigation into the phase relationships between different members of the paraffin series.

A part of this work dealt with the solubility of 32 in various lower members of the normal, straight-chain aliphatic series.[24] It was discovered that the freezing-

point curves of dicetyl in propane and butane showed a change in curvature at approximately 15°C below the melting point of the dicetyl.[25] This deviation was attributed to the fact that dicetyl existed in at least two crystalline forms, and it was found necessary to obtain more precise information on the crystalline structure of the paraffin hydrocarbons.

Since variation in crystalline structure was known to be accompanied in many cases by variation in density, it was decided to study the change of density of the pure paraffin members with change in temperature. The dilatometric method seemed to be best suited for this purpose. The investigation into the density and transition points of the higher aliphatic hydrocarbons was begun by Morris[10] and continued by Yatabe[32] and Patterson[20].

MATERIALS USED

Synthesis:

It was necessary first of all to obtain individual members of the series in as pure a state as possible. The homologues studied thus far have been 16-34 inclusive for the even members, and the single odd member 29. The source of each specimen used, together with details of purification, are given in Appendix I.

Purification:

In the case of practically all the hydrocarbons synthesized in this laboratory, the first step in purifi-

cation was to heat the crude product with small portions of concentrated sulphuric acid at 130°C, following the method of Piper[22]. The sulphuric acid quantitatively removed ketones and alcohols. In general this treatment tends to raise somewhat the melting point of the sample. Because the fatty acids are soluble to an appreciable extent in sulphuric acid, whereas theoretically the hydrocarbons are not, this treatment should also be effective in removing any fatty acid impurity remaining from the Peterson synthesis.(cf. p.) The melting points of the paraffins being somewhat higher than those of the corresponding fatty acids from which they are made, it is reasonable to suppose that removal of any acid impurity present would raise the melting point of the hydrocarbon.

In practice it is found that there is considerable loss of hydrocarbon in the hot, concentrated sulphuric acid. Piper mentions a loss up to 20%, but in the case of 20 at least, the loss was closer to 50% before completely char-free sulphuric acid was obtained upon heating with the hydrocarbon. In the case of 18 the hydrocarbon was considered too valuable to risk losing all or any part of it in this was; in consequence it was not treated with sulphuric acid.

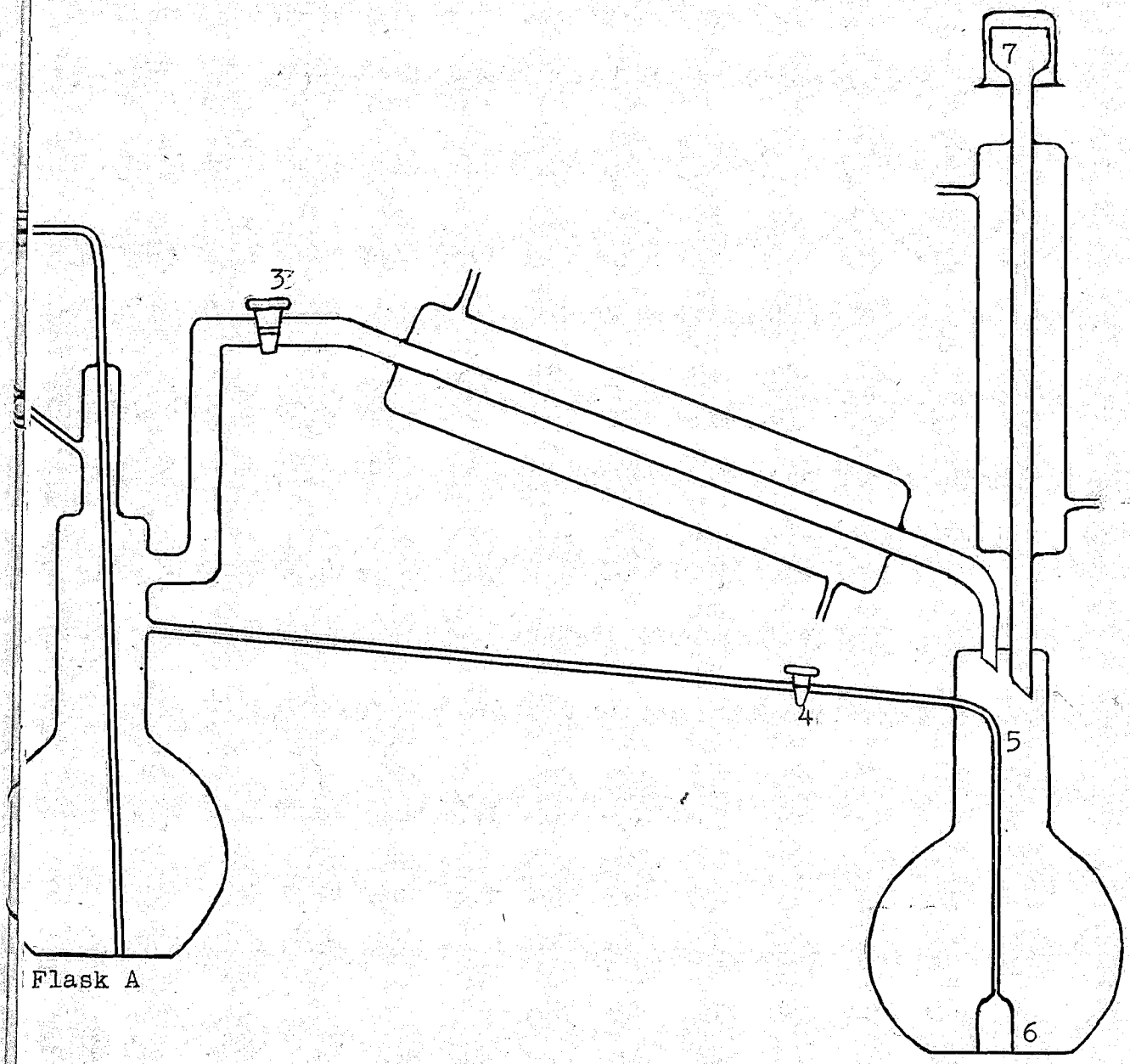
For those paraffins synthesized by a Grignard reagent, Oldham and Ubbelohde[17] suggest that a more rapid

purification can be effected by heating the paraffin with 20% oleum at 100°C until the test for halide is negative, then heating for a short time with concentrated sulphuric acid at 130°C in order to remove any sulphonic acids present.

Following is a description of the general method and apparatus used in the purification of many of the homologues investigated. The method described was employed for 18, 20, 26, and 34.

The most common method of purification involves the recrystallization of the hydrocarbon from some solvent such as acetic acid, ethyl alcohol, or ether. Acetic acid is considered to be the best solvent, because the higher members of the paraffin series are only slightly soluble in glacial acetic acid at boiling temperatures, and almost completely insoluble in the acid at room temperatures. The larger the volume of solvent used for a given weight of hydrocarbon, the greater will be the amount of soluble impurity removed. In practice the paraffin is dissolved in hot, glacial acetic acid by refluxing to the extent of from 1-3 grams of hydrocarbon per liter of acid. Upon cooling, the hydrocarbon crystallizes out in a mass of small, white needles. This procedure is repeated until the sample gives a constant melting point.

In some cases it was found necessary to repeat the crystallizations as many as twenty times, the final melting



Purification Apparatus

FIGURE I

point being approached assymptotically. In order to facilitate the operation and to reduce the possibility of contamination from outside sources, the apparatus shown in Figure I was devised and blown from pyrex glass.

Two 6-liter flasks are connected as shown across a condenser. The hydrocarbon to be purified is dissolved in pure glacial acetic acid and poured into flask B through the condenser under vacuum applied through 1 and 3. If this method is not practical, then B is filled with the acid and the soled hydrocarbon is dropped down through the condenser. Flask B is then heated and the mixture is allowed to reflux for several hours. By this method it was possible to purify up to 50 grams of the hydrocarbon at one time.

The acid was allowed to cool to room temperature, whereupon the hydrocarbon crystallized out and collected as a diffuse white, cloud-like layer on top of the acid.

The section marked (6) in figure I consists of four inches of 1-inch bore pyrex glass, joined on to $\frac{1}{4}$-inch bore tubing. This tubing is connected through stop-cock 4 to flask A. The expanded section 6 is filled with acid-washed glass wool and so packed as to provide a filter for the hydrocarbon crystals and whatever soluble or insoluble impurity might be with the sample being purified. With stopcocks 3 and 2 closed, suction is applied through 1, transmitted through stopcock 4, through 5 and 6 to the bottom of flask B. When

all the mother liquor has been drawn into A from B, stopcocks 2 and 4 are closed, 3 is opened, and heat is applied to flask A. Acid is distilled into B until one or two inches remain in the bottom of A.

With successive cycles of operation the hydrocarbon in B becomes cleaner and the acid in A becomes dirtier. At regular intervals a sample of hydrocarbon is withdrawn from B. This is done as follows: when all but 50-100cc of acid has been suctioned into A, a long glass tube is inserted in to B through the mouth of the condenser at 7, through which several cc of acid and crystals are drawn off. The crystals are filtered off, washed thoroughly with distilled water, dried, and a melting point determination is made.

When the hydrocarbon is considered sufficiently pure, as indicated by constant melting point, stopcocks 3 and 4 are closed, pressure is applied through 2, and the dirty acid is discharged through 2. The cold acid, which by this time contains megligible soluble impurity, is drawn from B into A, heated in order to ensure complete cleansing of A, and as before, blown out through 1. Flask B is then refilled with fresh acetic acid, heated to boiling, and the entire contents of the flask, that is, acid and whatever liquid hydrocarbon was not taken into solution during the refluxing, are drawn over into A. From there they are drawn or blown directly into a receiving flask. All passages are

cleared of hydrocarbon by drawing hot acid washings down through 7, up through 6, 5, and 4, and out at 1.

The method was found to be slow in the case of 34, as the higher members of the series are increasingly insoluble in acetic acid. Carothers[3] made use of the following solvents for the purification of higher aliphatic members:

Member	Melting Point	Solvent used for Crystallization
20	35.0- 35.6	Absolute Ethyl alcohol
30	65.0- 66.0	Absolute Ethyl plus Ethyl Ether
40	80.5- 81.0	Ethylene Chloride
50	91.9- 92.3	Ligroin plus Petroleum Ether
60	98.5- 99.3	Butyl Acetate
70	105. -105.5	Butyl Acetate

Table I.,

A slight modification in the above method of purification was necessary for the lower members such as 20. In this case the hydrocarbon was too soluble in the acid at room temperatures to effect a good separation of crystals, so flask B was kept under a spray of cold water after refluxing.

The above method made it possible to keep the hydrocarbon from the air and other possible sources of

contamination during purification. The sources of contamination were thus reduced to the apparatus itself, the reagents used, and subsequent treatment of the hydrocarbon.

The first source was eliminated insofar as possible by cleaning the apparatus successively with dichromate solution, distilled water, and acetic acid. In order to eliminate the possibility of contamination from the vasseline used on the stopcocks, several liters of hot acetic acid were drawn through all stopcocks, before the hydrocarbon was introduced into the flask.

The second source of contamination, namely, the acid itself, could never be completely controlled. In the case of one sample of 34, the specimen being purified had a decidedly yellow tinge which was not removed by forty crystallizations. The acid residues were removed several times, but each time after several distillations the residues were yellow in color. In this case it was suspected that either all the acid used was contaminated, or in some manner decomposed upon repeated heating. It may be mentioned that this particular sample of 34 was never obtained colorless, and in the dilatometer gave a setting point of 71.5, which is several degrees lower than the accepted value. (cf p.38)

The question arose as to whether or not this method of purification could be used to advantage on quantities of material greater than that soluble in boiling acetic acid.

The refluxing ensures intimate contact between the hydrocarbon and the acid, and in spite of the fact that it was no longer a matter of straight recrystallization, it was believed that considerable quantities of pure paraffin could be obtained by this method regardless of whether or not all the hydrocarbon actually had been taken into solution and crystallized out.

EXPERIMENTAL PROCEDURE

The apparatus and technique used by all investigators in this work have been essentially the same. For this reason only a rough outline of the equipment and procedure followed is given, except for those details which are considered of importance and have not appeared elsewhere.

Temperature Control:

The constant-temperature bath used[10] consisted of a large glass container equipped with stirrer, variable heating coil, stand for dilatometer bulb, circulation apparatus for cold water, facilities for keeping the level of water constant in the bath, and thermoregulator.

Originally it was the practice to change the sensitive liquid[20] in the thermoregulator bulb whenever required. The author found it more convenient to arrange a complete series of sensitive liquids covering the range from 15-90°C in approximately 5°C intervals. Once made, these tubes could be placed in the circuit whenever needed, and could be used

indefinitely, thus saving on time and materials.

The sensitive liquid control is dependent upon barometric pressure, and the temperature of the bath was found to fluctuate if left unattended, but by careful manual control it was possible to maintain any temperature in the range 20°-80° to within 1/50 of a degree for as long a period as desired.

The total range covered was from 0-95°C, the highest temperature obtainable with the bath used. By using a high boiling-point liquid in the bath (glycol, for example) and with a slight modification of the dilatometer tubes to take care of the increased volume needed for the added expansion of the hydrocarbon, the density curves could be investigated at higher temperatures.

Dilatometer Tubes:

Some difficulty was encountered in placing the sample in the dilatometer bulbs. From a piece of small-bore thin-walled glass tubing is drawn a tiny funnel as shown. This funnel is cut off to such a length as will just clear the dilatometer bulb stem.

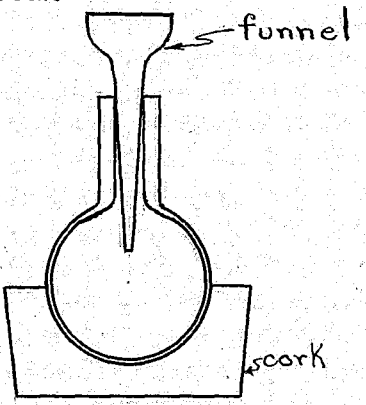


Figure II.

The bulb, funnel and cork are placed in an oven at 100°C, and the liquid sample is poured in. The entire unit is withdrawn from the bath with as little disturbance as possible and the hydrocarbon is allowed to solidify. An ice bath may be used if necessary. The filter is then withdrawn, if possible in such a manner that it does not touch the walls of the stem. If this is not possible, then a certain amount of hydrocarbon will cling to the walls of the dilatometer bulb stem. To remove this, the bulb is inverted (freezing the hydrocarbon if it is liquid at room temperature), and a small twist of clean paper used to remove all trace of hydrocarbon from the walls. During the course of this and subsequent operations, the hydrocarbon should be protected as much as possible from the atmosphere.

A complete description of the method of preparing the dilatometer bulbs and tubes is given by Patterson.[20]

Calibration of the tubes:

The theory of the determination of absolute density is relatively simple. A weighed sample of pure hydrocarbon is placed in a bulb attached to a capillary stem. A weighed amount of Hg is placed in the remainder of the bulb, and its height is measured above a fixed reference point on the stem at some fixed temperature. This gives us the weight of mercury alone, and, the specific volume of mercury being accurately known, its volume at the temperature required. By removing

the hydrocarbon and replacing it with mercury, measuring the height at the same temperature and making corrections for the expansion of the glass, we can obtain the volume of the mercury plus hydrocarbon. Subtracting one from the other gives the volume of hydrocarbon alone, and dividing into the weight gives the density.

By measuring capillary heights at various temperatures and making the necessary calculations, we can obtain temperature-density curves. The shape of the curve obtained indicates the changes of crystalline structure with temperature. A sample of the calculation necessary for calibration of the tubes and conversion of capillary heights to densities is given in Appendix II.

For the convenience of anyone who might be making the same calculations, which are somewhat tedious, the specific volume of mercury at one degree intervals in the range 0-100°C. is given in Appendix III.

MELTING POINTS OF THE NORMAL STRAIGHT CHAIN HYDROCARBONS

During the course of the investigation into the temperature-density curves, it was found feasible at the same time to study the melting-point relationships of the normal straight-chain paraffin series.

A survey of the literature reveals that considerable variation may exist in the melting-point values given for any

was reached within a few minutes, but not so in the curves sections A^1-B and B^1-C. As the regions of sharp transition were approached, the time required for the mercury level to reach a constant value increased rapidly. In the 0.1-0.2°C interval between t_1 and t_2 (that is, at a temperature just below the setting point) it required from one to two weeks for equilibrium to be established. During this time it was necessary to control the temperature as closely as possible. In actual practice, due to the necessity for leaving the bath unattended overnight, the temperature varied by as much as 0.5°C.

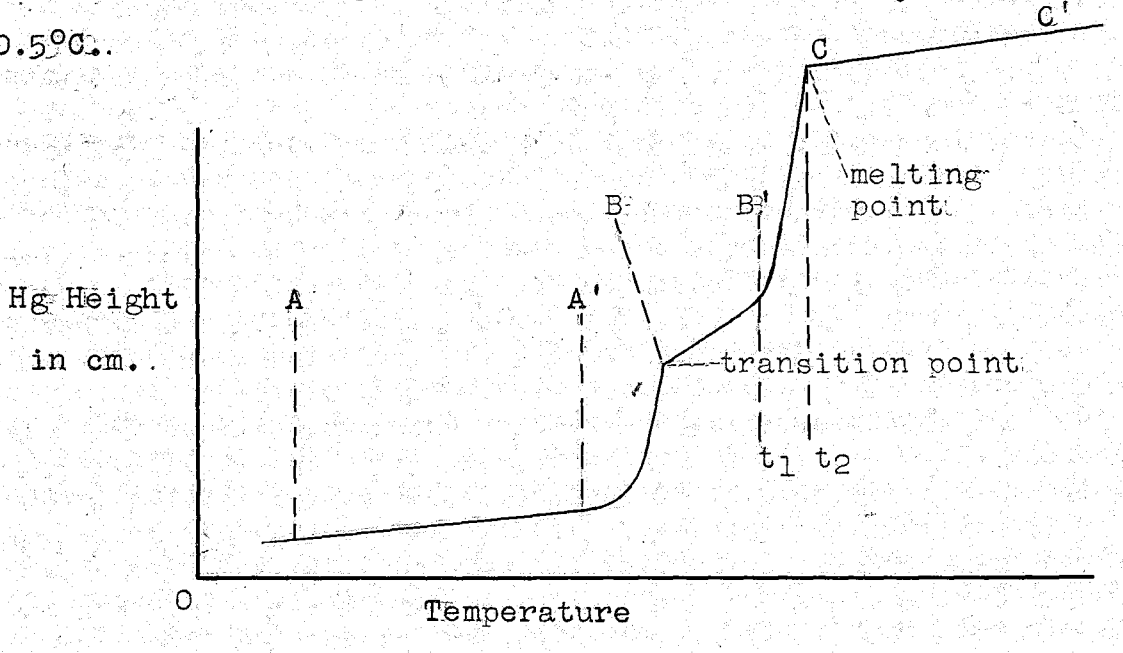


Figure III.

When the highest possible mercury level had been reached, the temperature was lowered by suitable increments, readings taken, and the values plotted in order to provide a check on the previous curve. It was found that on a descending temperature scale, the point C for any given sample

The capillary heights were plotted immediately as found. This was done for two reasons. The capillary height-temperature curves will be close in shape to the density-temperature curve, and therefore any discrepancy in the latter (due to impurity, say) will show up at once in the latter. Further, the capillary height-density curves show at a glance the temperature at which any transition points occur and thus indicate what regions must be reinvestigated. The general method of obtaining these curves follows.

After the tubes had been placed in the constant temperature bath, the height of the mercury column in the dilatometer stem above a fixed zero clip was plotted against temperature. The general form of the curve obtained is shown in Figure III, where B represented the first transition point and C the second transition or melting point.

Readings were begun at 0°C. The bath was kept at this temperature until a constant reading of the mercury level had been obtained; the temperature was then raised several degrees and held constant until equilibrium had been reached. The process was repeated at temperature intervals sufficiently close together to ensure a smooth and continuous curve. The curve given in Figure III is an idealized form of the curve for all members of the aliphatic series greater than 18 and less than 44.

In the regions $A\text{-}A^1$, $B\text{-}B^1$, and $C\text{-}C^1$, equilibrium

n	Melting Points, Observed by		
	This Lab.	Hildebrand	Piper
16			
18			
20	36.4	36.5	
22	44.0	44.0	
24	50.9	51.0	
26	56.0	57.0	56.4-56.6
28	61.4	62.0	61.4-61.5
29	63.5	64.0	63.4-63.6
30	65.7	66.0	65.6-65.8
32	69.8	70	69.5-69.7
34	72.9	73.5	

Table II.

setting point, obtained upon cooling, as distinguished from the melting point, obtained upon heating, for purposes of establishing the purity of the members under investigation. Where the exact melting point was found to be somewhat indeterminate, or at least variable, with observer and rate of heating, the setting point, determined by the appearance of the first crystal upon slow cooling, could be reproduced to within 0.2-0.1°C for any one sample. As can be seen from the density temperature curves, the same transition values were obtained upon heating or cooling with all members except 16 and 18, and in the case of these members the higher value is taken as being in best agreement with values obtained from other sources..

one hydrocarbon. Hildebrand and Wachter[8], for example, found that the melting-points recorded for 32 varied from 68°C. to 75°C. Selecting the best values available in the range 19 to 38, they plotted the number of carbon atoms against the melting point, and from the resulting curve, suggested a set of values in the range 19 to 36. This method is probably as satisfactory as any, so long as the melting points vary regularly with the number of carbon atoms, and provided there is no alternation between the melting points of the odd and even members of the series in the range considered. It was our purpose to extend the above correlation, and to discover what irregularities, if any, existed.

The purity of the samples used in this work was first determined by the constancy of the melting-point, determined by the method of Piper[22]. The values obtained are given in Table II, together with the corresponding values according to Hildebrand, and those given for the same members by Piper.

All the values obtained except that for 22 are lower than those suggested by Hildebrand, but they are in good agreement with Piper's values. As pointed out by Piper the slow heating used in his method results in values 0.4-0.7° lower than those obtained by the usual method of melting point determination.

In our work it was found advisable to use the

could be determined with an accuracy limited only be the rigidity of temperature control, the accuracy of temperature measurement, and the patience of the observer.

In the case of 20, for example, an initial determination fixed point C between 36°C and 37°C. The temperature was raised to approximately 50°C (that is, well above the melting point) and readings retaken along C'-C. The temperature was lowered by 0.1°C increments below 37°C, and C was found to lie between 36.2 and 36.3°C. The temperature was once more raised well above the melting point and C'-C retraced to 36.3°C. The temperature of the bath was held constant at 36.3°C for half an hour, during which no change in the mercury height could be observed. The temperature was then lowered by 0.02°C increments and kept constant at each point until it was certain that the height did not change.

This procedure was repeated until the temperature had been lowered to 36.22°C. While the temperature was dropping from 36.24 to 36.22°C, the level in the dilatometer tube wavered for a few seconds and then suddenly dropped. With the temperature being maintained at 36.22-36.20°C for two days, capillary heights were recorded at regular intervals until equilibrium had been reached.

Table III gives the values obtained just below the first transition point (cf. p. 14) for 22, and these figures

are plotted in Figure IV.

Capillary Height	Time
29.70	1 min
28.95	2 "
28.42	5 "
27.72	10 "
26.08	20 "
25.68	30 "
24.80	40 "
24.10	50 "
23.48	60 "
22.36	80 "
21.45	100 "
20.60	120 "
18.68	3 hours
17.34	4 "
16.20	5 "
15.03	6 "
14.75	7 "
14.30	8 "
14.00	9 "
13.92	10 "
13.89	15 "

Table III

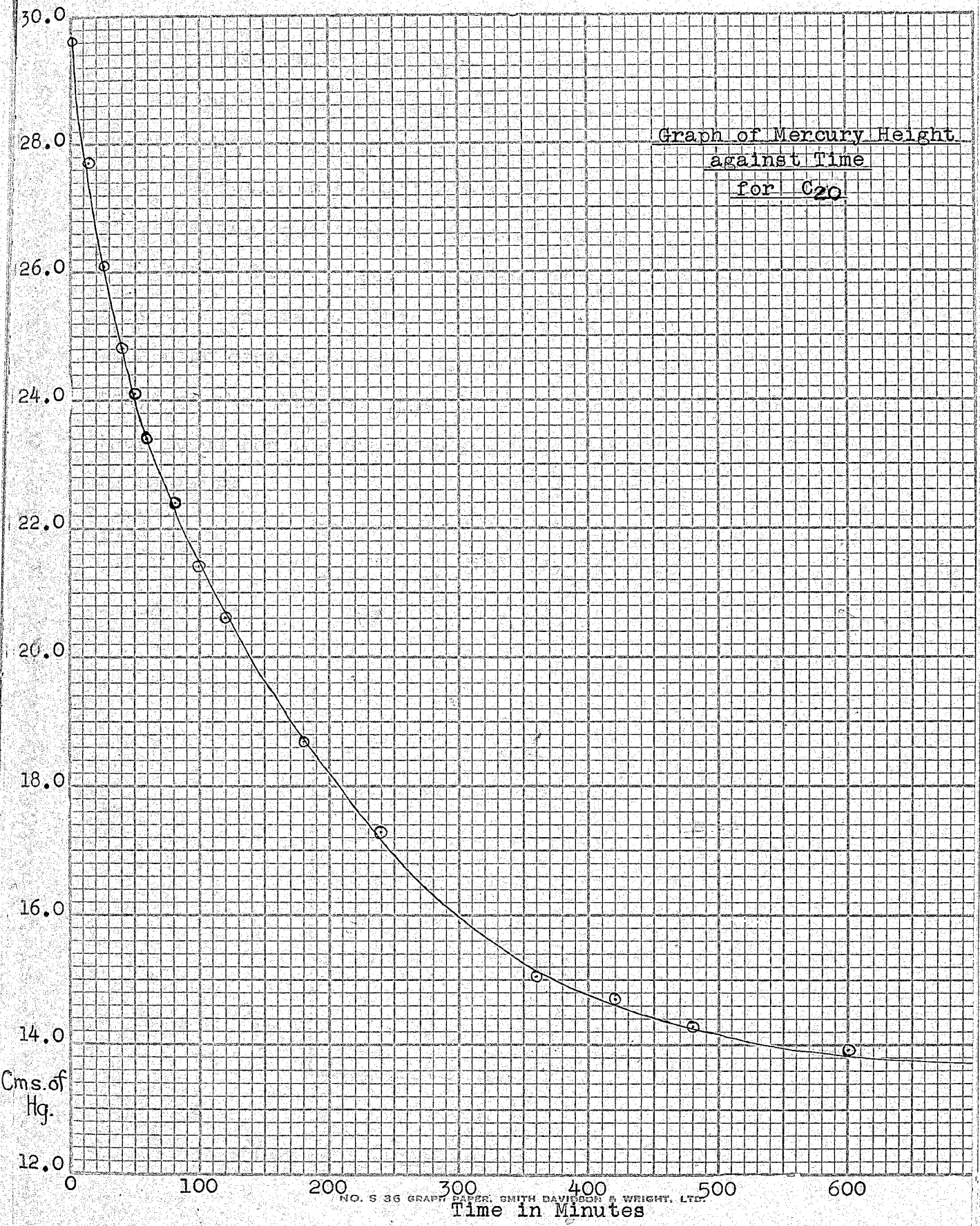

Graph of Mercury Height against Time for C_{20}
30.0
28.0
26.0
24.0
22.0
20.0
18.0
16.0
14.0
12.0
Cms. of Hg.
0
100
200
300
400
500
600
Time in Minutes

FIGURE IV.

It can be seen that considerable time is required for the hydrocarbon to reach equilibrium at the transition point under conditions of constant temperature. The curve is assymptotic to a capillary height of 13.85 cms, this value representing equilibrium. In the case of 20, point C was determined three times, the values obtained agreeing within 1/50 of a degree C. This point, being fixed, determinable to a high degree of accuracy, and exactly reproducable, is taken as the setting point for 20. The corresponding values thus found for the other hydrocarbons investigated are given in Table IV.

n.	Setting Point
16	18.3
18	27.6
20	36.2
22	44.1
24	50.7
26	55.8
28	61.2
29	63.2
30	65.4
32	69.5
34	72.9

Table IV

As has been shown, these setting points are

reproducible with a high degree of coincidence for any given sample. The same high degree of reproducability is not obtainable, however, with different specimens of the same member. In the case of 32, for instance, two different samples from two different sources, supposedly of an equal degree of purity were used; the melting points found in Piper's apparatus checked within 0.2°C, but the setting points obtained by the dilatometer method varied by 0.5°C. It may be assumed that thid difference in melting point was due to difference in purity. 22 was similarly checked, using two samples made from the same acid by identical methods of synthesis, purified in the same manner, and enclosed in almost identical tubes, but even here the melting points varied by 0.2°C.

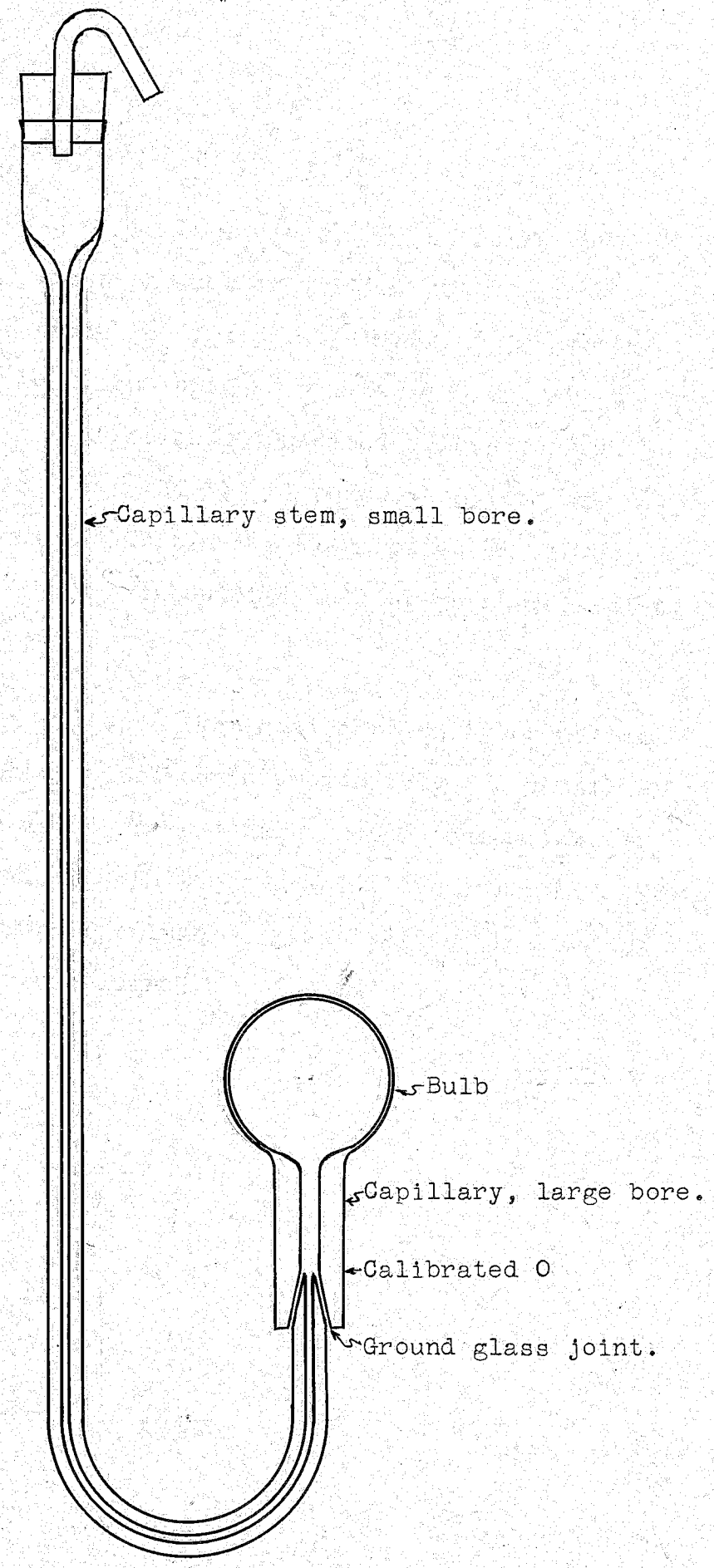
It was therefore assumed that the hydrocarbons were not sufficiently pure to warrant recording their setting points to within more than 1/10°C. Particular are was taken in the purification of theyhydrocarbon samples, but there still remains possibility of contamination.....from the materials used in the synthesis and not completely removed during purification, from the chemicals used in purification, or possibly introduced while setting up the dilatometer bulbs. Nevertheless, we believe that the dilatometer method described here can be refined to provide means of determining melting points within any desired degree of refinement, and should be seriously considered as a means for determining microanalytically the melting points of such homologous series as the

paraffins, fatty acids, alcohols, etc.

A determination of the setting point for 22 as described above took at least two weeks, and this fact would made the procedure as outlined prohibitive in many cases. However, a dilatometer tube similar to the one shown in Figure W might be used to shorten considerably the time of melting-point or setting-point determination.

The sample to be tested could be placed in the bulb and kept in a molten state while the mercury was poured in to fill completely the bulb and enlarged stem. The bulb could then be placed on ice, and mercury added as needed, so that at some reference temperature, say 0°C, the mercury would be levelwwith the graduation on the dilatometer stem. With the stem inserted and the mercury seal filled, the completed dilatometer tube would be ready to be placed in a constant temperature bath. If the melting point were known within a degree or so, it should be possible to determine the true melting point to any desired degree of accuracy within a few hours.

In correlating the melting-points of the normal paraffin series, we attempted insofar as possible to select values obtained by one set of workers. For this purpose we have used the selected values of Deanesly and Carleton[5] for the range 6-18, and our own from 18-34. For 40, 50, 60 and 70 we selected the melting points given by Carothers[3], and



Proposed Dilatometer Tube

FIGURE V.

for 36, 52, 62, and 64, those of Gascard.[77]

No single curve could be found to fit the entire series, which is shown plotted as melting point versus number of carbon atoms in Figure VII. Moullin[11] suggested that the single equation $\log(n-2) = 1.065 + 5.29t/10^3$ could be used. From this equation he obtained values for melting points calculated from 3 to 31. A comparison with the values from the International Critical Tables, selected values, together with Moullin's calculated melting points, is given in Table V.

Moullin suggests that a discontinuity occurs at n=28, the line being displaced approximately 3°C parallel to itself. This is scarcely borne out by a comparison of the calculated values with the suspect International Critical Tables values given in column 3, even less so with the selected values given in column 5.

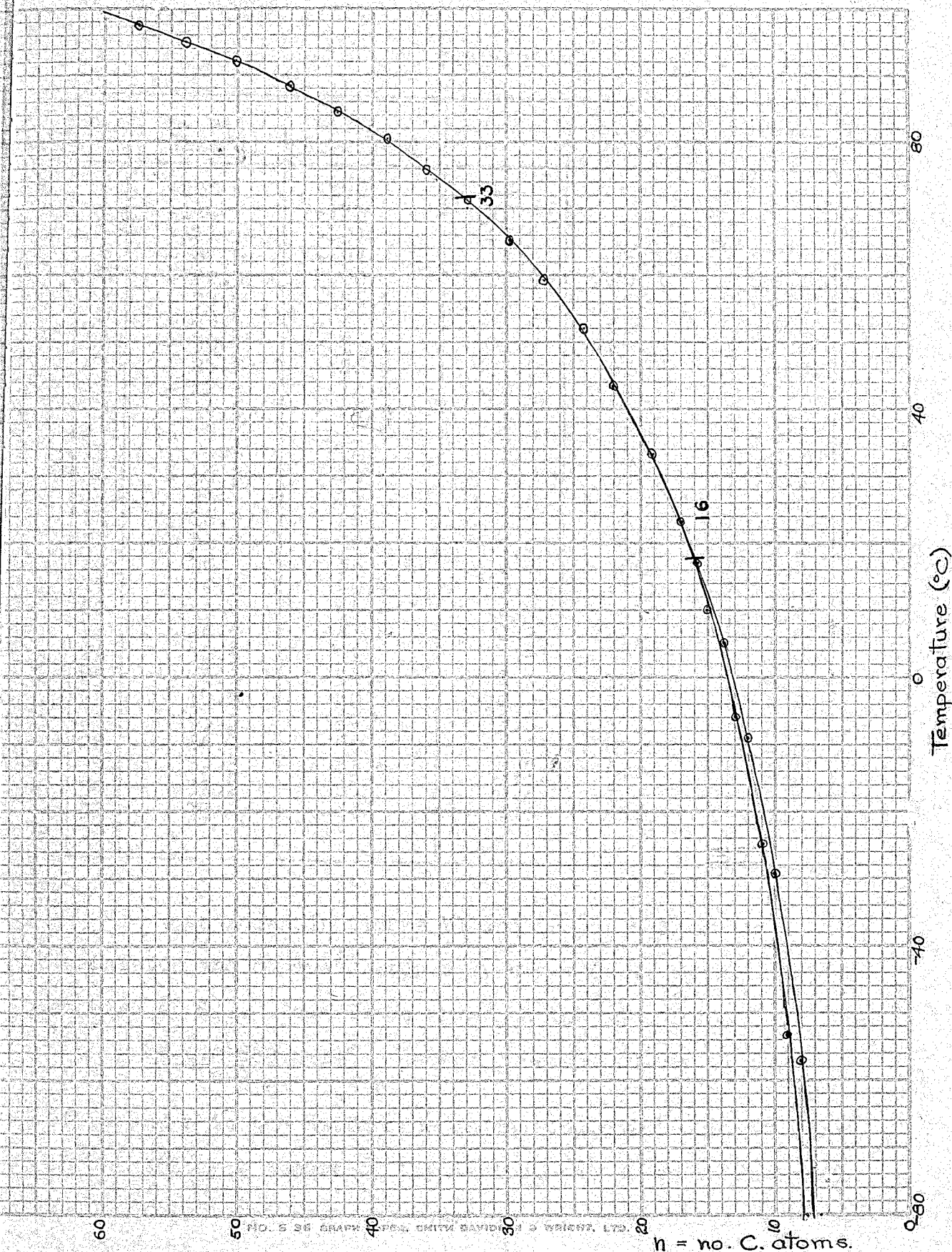


FIGURE VI

Table V

n.	m. p. (Calc'd)	m. p. (1926ICT)	Dev.	m. p. (Selected)	Dev.
3	-200	-190	-10		
4	-145	-135	-10		
5	-111	-131	20		
6	- 87.5	- 94	6.5	-95.3	7.8
7	- 69.5	- 90	20.5	-90.6	21.1
8	- 54.5	- 56.5	2	-56.8	2.3
9	- 43.5	- 51.0	7.5	-53.7	10.2
10	- 30.7	- 32.0	1.3	-29.7	-1.0
11	- 21.0	- 26.5	5.5	-25.6	4.6
12	- 12 5	- 12.0	--0.5	- 9.6	-2.9
13	- 4.6	- 6.2	1.6	- 6.0	1.4
14	- 2.7	5.5	- 2.8	5.5	-2.8
15	9.3	10	- 0.7	10.0	-0.7
16	16.3	20	- 3.7	18.1	-1.8
17	21	25	- 1.5	22.0	-1.0
18	26.3	28	- 1.7	28.0	-1.7
19	31.2	32	- 0.8	31.4	-0.2
20	36	38	- 2.0	36.2	-0.2
21	40.5	40.4	0.1	40.4	0.1
22	44.6	44.4	0.2	44.0	0.6
23	48.6	47.8	0.9	47.0	1.6
24	52.5	51.0	1.5	50.6	1.9
25	56.1	54.0	2.1	53.3	2.8
26	59.6	60	- 0.4	55.8	2.8
27	63.0	59.5	3.5	59.1	2.9
28	66.2	65	1.2	61.2	4.0
29	69.3	63.6	5.7	63.2	6.1
30	72.2	66	6.2	65.4	6.8
31	75	68	7.0	68.0	7.0
32					

As shown in figure VI and as pointed out by Tsakalotos and others[31], the n-mp curve is irregular at least as high as C_{15}. Tsakolotos proposed the equation

$$t = \frac{85-0.01882(n-1)^2}{n-1}$$

where n is the number of carbon atoms and t is the difference in melting point between n and the next lowest member of the series. As shown in Table VI, values calculated from his equation are in excellent agreement

from 16 to 35 with values taken from Krafft[33] (from which the original equation was derived), and with the single value of 60 taken from Hell and Hagelle[34].

n	m. p. Tsak.Eqn.	m. p. Krafft	Dev.	m. p. Selected	Dev.
16	17.1	18	-0.9	18.1	-1.0
17	23	22.5	0.5	22.0	1.0
18	27.7	28.0	0.3	28.0	-0.3
19	32.0	32	0.0	31.4	-0.6
20	36.2	36.7	-0.5	36.2	-0.0
21	40.1	40.4	-0.3	40.4	-0.3
22	43.7	44.4	-0.7	44.0	-0.3
23	47.2	47.7	-0.5	47.0	0.2
24	50.4	51.1	-0.7	50.6	-0.2
25	53.5			53.3	0.2
26	56.4			55.8	0.6
27	59.8	59.5	0.3	59.1	0.7
28	62.4			61.2	1.2
29	64.9			63.2	1.7
30	67.3			65.4	1.9
31	69.0	68.1	0.3	68	1.0
32	71.2	70.5	0.7	69.5	1.7
33	73.3			72.0	1.3
34	75.3			73.5	1.8
35	77.0	74.7	2.3	75	2.0
36	78.8			76	2.8
60	101.5	101.0-5		98.9	2.6

Table VI

A comparison of the calculated values with those selected in this work, however, shows that although the agreement is excellent from 16 to 25, a definite and almost constant deviation is shown for members greater than 28.

Garner[6], from a plot of Q/T versus n and Q versus n for the hydrocarbons 22, 26, 30, 34, obtained the

equations:

$$Q/T = 0.001991n - 0.00404$$

and

$$Q = 0.6085n - 1.75$$

where Q = heat of transition

and T = absolute temperature of transition.

Eliminating Q gives the equation:

$$T = \frac{0.6085n - 1.75}{0.001491n - 0.00404}$$

He used this equation to obtain the setting points of the hydrocarbons from 5 - 70. The values thus calculated are compared with the final selected values (cf page 38) in Table VII.

Considering the small number of paraffins used to obtain the equation, melting points derived from it are in fairly good agreement with the selected values throughout the entire range. In the case of the above members, ie 22, 26, 30, and 34, agreement is within 0.2°C.

Figure VII shows a plot of the selected values a against log(n-2). From Figure VII four equations have been obtained, and these equations, together with the malting points calculated from and the difference between selected and calculated values are given in the following sections.

n	m. p. Calc'd	m. p. Selected	Dev.
6	-126.7	- 93	-33.7
7	- 99.1	- 89.7	- 9.9
8	- 77.8	- 56.7	-21.1
9	- 59.6	- 54.1	- 5.5
10	- 44.2	- 29.7	-14.5
11	- 31.1	- 27.6	- 3.5
12	- 19.8	- 10.0	- 9.8
13	- 9.9	- 6.3	- 3.6
14	- 1.3	5.5	- 4.2
15	6.4	10.5	- 4.1
16	13.3	18.0	- 4.7
17	19.7	22.5	- 2.5
18	25.0	28.3	- 3.3
19	30.0	32.0	- 2.0
20	34.7	36.2	- 1.5
22	43.0	43.2	- 0.2
26	55.6	44.4	0.1
30	65.6	65.7	- 0.1
34	73.0	73.0	- 0.0
35	74.7	74.4	0.3
36	76.2	75.6	0.6
40	81.6	80.4	1.6
50	92.0	90.6	1.4
54	94.9	94.0	0.9
60	99.9	99	- 0.2
62	100.5	100.5	- 0.6
64	101.0	102	- 1.0
70	104.2	105.4	- 1.2

Table VII

The equation $\log(n-2) = 1.067 - 0.00410t$ was found to correlate most satisfactorily the members 7-9-11-13-15-16.

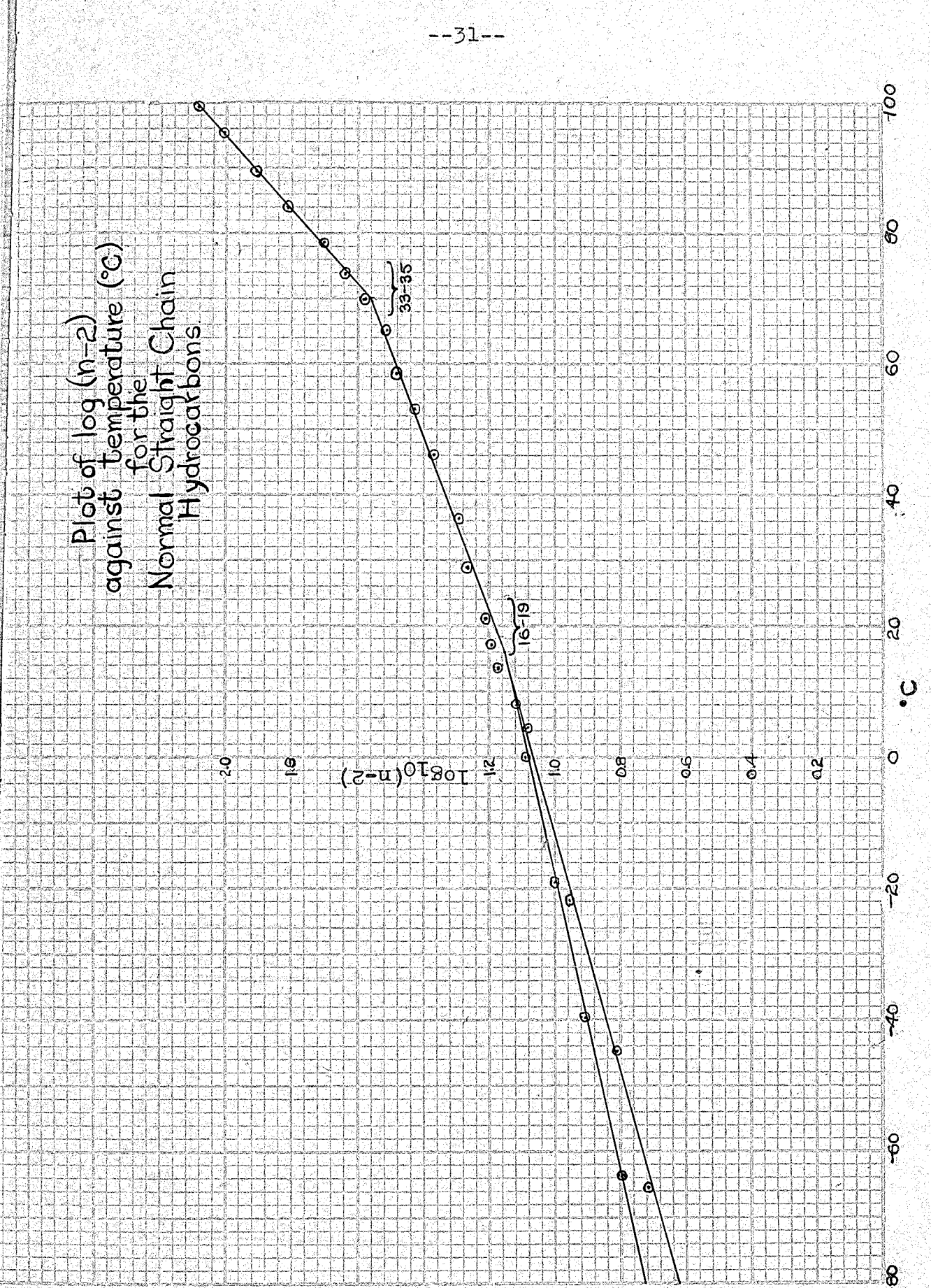

Plot of log (n-2) against temperature (°C.) for the Normal Straight Chain Hydrocarbons.
log10(n-2)
°C.
100
80
60
40
20
0
-20
-40
-60
-80
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
33-35
19-21

FIGURE VII

n	m. p. Calc'd	m. p. Selected	dev.
7	-89.7	-90.6	0.9
9	-54.1	-53.7	-0.4
11	-27.6	-25.6	-2.0
13	- 6.25	- 6.0	-0.3
15	11.4	10.0	1.4
16	19.3	18.1	1.2

Table VIII

The calculated values are fairly close to the observed values, except in the case of C_{11}. Members lower than C_6, for both the odd and even members, are not included, as the deviation of observed from calculated melting points are too great.

For the even members 6-8-10-12-14-16, the best equation was found to be $\log(n-2) = 1.051 - 0.00481t$.

n	m. p. Calc'd	m. p. Selected	dev.
6	-93.3	-95.3	2.0
8	-56.7	-56.8	0.1
10	-29.7	-30.8	-1.1
12	- 9.6	-10.6	-1.1
14	5.5	5.2	0.3
16	19.3	18.1	1.5

Table IX

Here again the correlation is fairly good, apart from C_6. The 1941 edition of Hydrocarbon Constants[35] gives the melting point of C_6 to be -94.5, which would reduce the deviation to 1.2°C, but there is no reason to assume that this latter value, taken from Parks[19], is any more reliable than that of -95.3, obtained by Shepard[26].

It may be noted in reference to the melting-points recorded by Deanesly and Carelton, that C_{16} was used as a reference point, and that the properties of both C_{16} and C_{12} were carefully checked by them. Their melting-point values for C_{12} were -9.604°C ± 0.003, and for C_{16}, 18.145°C ± 0.003. It is possible to obtain an equation applicable to 10-12-14-and 16, giving deviations from observed values of less than 0.5°C, but C_6 would then be calculated 3.5°C too high. From Figure VII it can be seen that three of the lines converge in the neighborhood of C_{16}. Assuming that the break from one curve to another is not sharp, as shown, then the calculated melting-points for C_{16}, C_{17} and C_{18} will be too high. As shown in Table X, these three values are all calculated too high.

The range C_{16} to C_{34} is covered by the equation

$$\log(n-2) = 1.02 - 0.0065t$$

All of the calculated values between 19 and 29 are too low, and an equation can be obtained for this range with a maximum deviation of 0.5° as shown in Table XI.

n.	m. p. Calc'd	m. p. Observed	dev.
16	19.4	18.145	1.3
17	24.0	22.0	2.0
18	28.3	28.0	0.3
19	32.4	31.4	1.2
20	36.2	36.2	-0.0
21	39.8	40.4	-0.6
22	43.2	44.0	-0.8
23	46.5	47.0	-0.5
24	49.6	50.6	-1.0
25	52.5	53.3	-0.8
26	55.4	55.8	-0.4
27	58.1	59.1	-1.0
28	60.7	61.2	-0.5
29	63.3	63.2	-0.0
30	65.7	65.4	0.3
31	68.1	68	0.1
32	70.3	69.5	0.8
33	72.5	72.0	0.5
34	74.6	73.5	1.1
35	76.6	75.0	2.1

Table X

n	dev.
20	0.5
21	-0.1
22	-0.3
23	-0.00
24	-0.5
25	-0.3
26	0.1
27	-0.5
28	-0.0
29	0.5
30	-0.8
31	-0.6
32	-1.3

Table XI

However, the data used for the calculations shown in Table XI is not considered sufficiently reliable to draw any

conclusions from the small deviations thus obtained.

For the remainder of the series, from 33 up to 70,, was derived the equation:

$$\log(n-2) = 1.02 - 0.0065t.$$

n	m. p. Calc'd	m. p. Observed	Ref.	Dev.
28	64.0	61.2	**	2.8
29	65.6	63.3	**	2.4
30	67.2	66.4	**	1.8
31	68.7	68	36	0.7
32	70.2	69.5	**	0.7
33	71.6	72.0	8	-0.4
34	73.0	72.9	**	0.1
35	74.4	75	8	-0.6
36	75.6	76	8	-0.4
37	76.9	76.4	3535	0.5
38	78.0	77.6	3535	0.4
39	79.2	78.8	3535	0.4
40	80.4	80.7	3 3	-0.3
41	81.5	81.7	3535	-0.2
42	82.6	82.9	3535	-0.3
43	83.6	83.8	3535	-0.2
44	84.8	86.4	3 35	-1.6
50	90.6	92.1	7 3	-1.5
54	94.0	95.0	3 7	-1.0
60	98.7	98.9	7 3	-0.2
62	100.2	100.5	7 7	-0.3
64	102.2	102.0	33 7	0.2
70	105.4	105.3	3	0.1

** Values obtained in this laboratory.

Table XII

The closeness of the agreement to a general equation in this range is rather surprising. 44 and 50 show appreciable deviation, but out of 20 melting points compared, selected from half a dozen original sources, twelve of them are within 0.4°C of the calculated value, and 17 are within 0.7°C.

The apparent smoothness of this curve is all the more remarkable when it is considered how little work has been done on the higher members of the aliphatic hydrocarbons series, and how difficult it is to obtain the individual members in the pure form.

Included among the various attempts made to find relationships between the molecular weights and melting points of homologous series, Austen[1] proposes the equation:

$$\log M = A - 4t/10^4$$

where A is a constant dependent upon the series considered. Table XIII gives the value of A for the paraffin series, calculated for the melting points shown.

n	m. p.	A
20	36.2	2.3055
22	44.1	2.3160
24	50.7	2.3269
26	55.8	2.3400
28	61.2	2.3510
29	63.2	2.3580
30	65.4	2.3640
32	69.8	2.3750

Table XIII

The plot of A-n shown in Figure VIII shows that the variation of the constant is linear with the range considered and Austen's equation becomes:

$\log M = A - Bt - 4t/10^4$, where B is another constant. This equation, similar to all others proposed for homologous series, holds good only over a limited range of the total series.

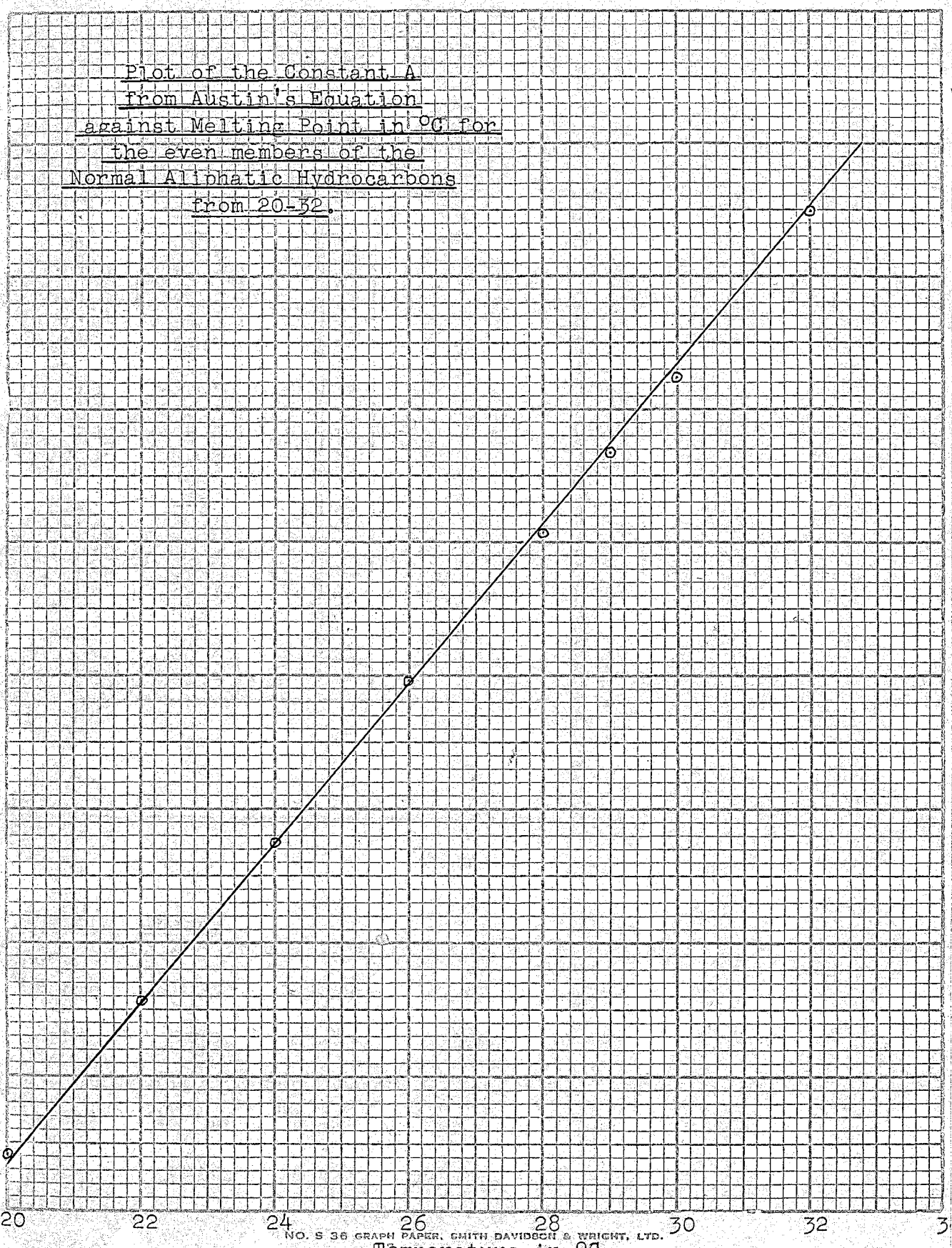

Plot of the Constant A
from Austin's Equation
against Melting Point in °C for
the even members of the
Normal Aliphatic Hydrocarbons
from 20-32.
39
38
37
36
35
34
33
32
31
A.
30
20
22
24
26
28
30
32
NO. S 36 GRAPH PAPER, SMITH DAVIDSON & WRIGHT, LTD.
Temperature in °C

FIGURE VIII

From the foregoing data and curve-fitting, we suggest the following values for the melting points of the normal straight-chain hydrocarbon members.

n	mp.	dev.	n	mp.	dev.	n	mp.	dev.
6	-93.0	1.0	26	55.5	0.3	46		
7	-89.7	0.5	27	58.1	0.5	47		
8	-56.7	0.3	28	60.7	0.5	48		
9	-54.1	0.3	29	63.3	0.3	49		
10	-29.7	0.5	30	65.7	0.3	50	90.6	0.2
11	-27.6	1.0	31	68.0	0.3	51		
12	-10.0	0.5	32	70.0	0.5	52		
13	- 6.3	0.3	33	71.6	0.4	53		
14	5.5	0.3	34	73.0	0.4	54	94.0	0.2
15	10.5	0.5	35	74.4	0.4	55		
16	18.0	0.2	36	75.6	0.4	56		
17	22.5	0.5	37	76.9	0.4	57		
18	28.3	0.3	38	78.0	0.4	58		
19	32.0	0.5	39	79.2	0.4	59		
20	36.2	0.2	40	80.4	0.4	60	99.0	0.2
21	39.8	0.4	41	81.5	0.4	61		
22	43.2	0.5	42	82.6	0.3	62	100.5	0.2
23	46.5	0.5	43	83.7	0.3	63		
24	49.6	0.5	44	84.8	0.3	64	102	0.2
25	52.5	0.5	45			65		
						66		
						67		
						68		
						69		
						70	105.4	0.2

Table XIV

General Theory

The normal aliphatic hydrocarbons being completely symmetrical and uninfluenced by the presence of polar groups, lend themselves to a study of atomic structure and molecular measurements. X-ray studies on the series, made by Saville[33], Müller[12-16], Piper[22] and others, have established the fact that many members of the paraffin series exist in several enantiotropic forms. These studies have shown that at the

point of transition from one crystalline form to another, there is a large change in the 001 lattice spacings with a relatively small change in the area of the basal plane. That is to say, in the change from one form to another there is a change in the density. Because of this fact, the density changes can be utilized in the determination of the temperature at which transition occurs. One of the objects of this work was a use of the dilatometric measurements as a means of throwing some light on the complex crystalline structure and crystal changes of the paraffins, as well as to find some relationship being density change and crystalline form.

There appears to be general agreement that the aliphatic hydrocarbons exist in at least three crystalline forms:

A form.

The chain axis is vertical to the 001 plane, and the planar spacings are a direct measure of the length of the molecules. Even members of 18 or more carbon atoms and odd members of 11 or more carbon atoms show this form

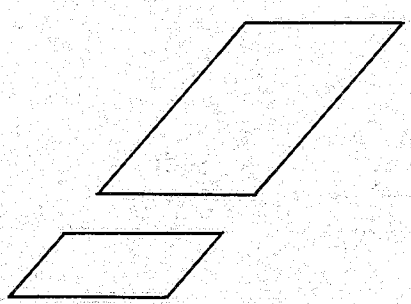
near the melting point (that is, in the transition region). Müller[13] gives the following 001 spacings:

n	A units
26	34.95
27	36.38
28	37
29	38.68
30	40.5
31	41.5
32	42.33
34	45.5
35	46.64
36	47.5

Table XV

From the above data it can be seen that the spacings are a direct measurement of the chain length.

B form:



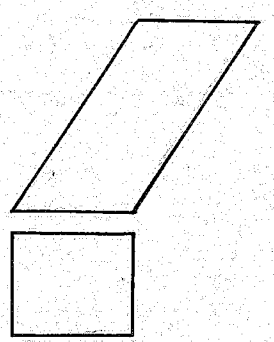
Even-numbered paraffins up to 24 at normal temperatures crystallize with the chain axes inclined at a constant angle to the 001 plane. The spacings, as given by Müller, are given in Table XVI.

n.	Å units
26	31
28	33.25
32	37.8
34	39.86
36	42.33

Table XVI

The 001 spacings of this modification are shorter than the A form of the transition region. On cooling, the hydrocarbons resume the B form.

C form:



26 is the only hydrocarbon that shows all three forms, and the value of the 001 spacing is given ad 32.6, that is, it shows a value lying between the other two spacings. The A form is supposed to be that form into which the odd-numbered members normally crystallize. The even-numbered members crystallize with a tilted C form, and show a higher transition temperature. This is borne out by the temperature-density curve obtained for 29 (cf page **68**), as contrasted with the curves obtained for the even members.

Odd-numbered paraffins never assume the C form.

In our work it was found that with some members the density curve obtained upon heating differed from that obtained upon cooling. Müller[14] obtained values for the long spacings; ie, those spacings dependent mainly on the length of the carbon chain. Two such values were recorded for 18 and 20. A similar phenomenon occurs with 22, values for which are not given.

n	d_1	d_2
18	25.3	23.3
20	27.4	25.4

The connection is not apparent, but the above spacings may account for the fact that 20 and 22 exhibit the same general density-temperature characteristics as 24, 26, etc., on a rising temperature scale, and they possess the same form as the lower even-numbered members on a decreasing temperature scale.

As the hydrocarbons are heated ϕ (Figure IX) approaches 60°, showing hexagonal close packing above the melting point. 18 and 20 do not reach the state at the melting point, whereas 22 does. This liquid crystalline condition may be an extreme case of molecular space arrangement in liquids, as suggested by Stewart[27] in his paper dealing with cybotaxis.

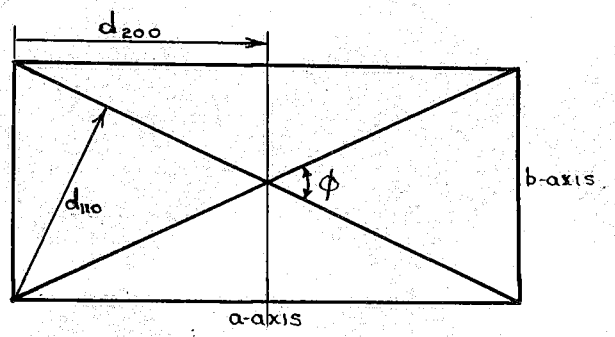
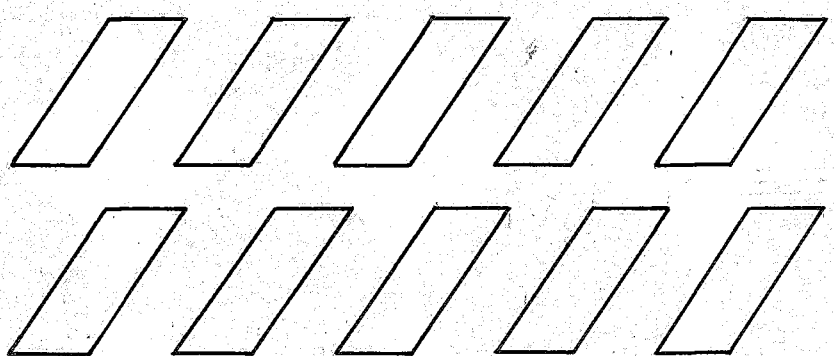


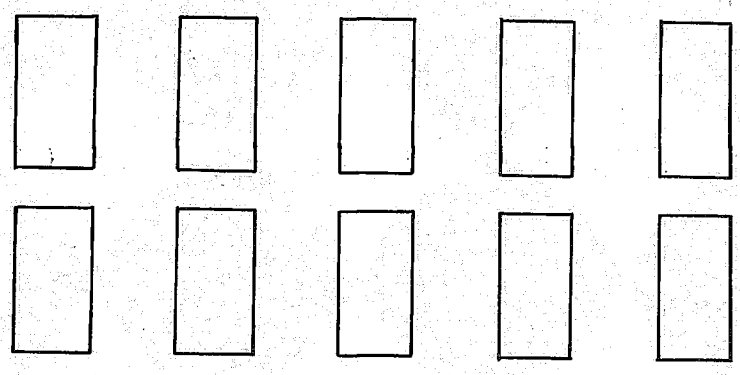
Figure IX

It is possible that above the melting point the hexagonal crystal arrangement of the paraffin molecules increases with temperature, and, on approaching the boiling point, the crystalline state gives way in a regularm manner to a state of random molecular distribution.

A relatively simple interpretation can be made of the change in density at the transition point. The hydrocarbon exists in the solid state as crystals of the B form.



When it is heated, the only change is a regular increase in the 001 spacing. When the first transition point is reached, the picture becomes



the volume occupied per molecule increases rapidly, and there is a sharp decrease in density. Throughout the transition region a rise in temperature is marked by cubical expansion only, with no change in crystalline structure (at least no structural change measureably effecting the temperature). At the melting point there is a uniform, rapid change to the hexagonal close packing above the melting point, and at the melting point there is a rapid decrease in density.

In the case of 20 and 22, where no transition was obtained upon heating, the C form passes over into the hexagonal form of the liquid state. Upon cooling from the liquid state, all members above 16 show the two transitions. This subject will be dealt with at greater length in the discussion of the individual hydrocarbons.

For the even-numbered paraffins greater than 16, as they are cooled from the liquid state, crystallization first takes place in the normal or A form. This A form contracts

with regularly increasing density until the second transition point is reached. It has not yet been determined exactly what change in the intermolecular and intramolecular forces involved causes this change into the stable A form. As the temperature decreases the density increases, the molecules come closer together, the forces of cohesion increase, and at the transition point the equilibrium existing before between these forces is destroyed and another crystalline form appears, either the B form or C form with tilted axis.

According to Piper[22] and Kolvoort[9], the lower transition point is more strongly affected by contamination than the upper. This is logical in view of the delicate equilibrium existing between opposing molecular forces.

RESULTS

Following are the results obtained. In the case of each individual hydrocarbon a graph is included, together with a discussion of the curve. In order to cut down the main body of this work, the actual densities are given in Appendix IV.

Hexadecane

The first sample tested was known to be impure (cf page 59), but for purposes of comparing it with other members of the series, it was decided to make the density calculations. No transition comparable to that found in the higher members was found. As seen from Figure X, two separate curves were obtained in the solid state.

The exact conditions by which one form is converted into the other could not be determined. The lower section (A) was obtained at least twice with the temperature going down. A region of instability was encountered with rising temperature at 12-13°C, and in an effort to find a smooth curve in this particular region, the temperature was held constant for as long a time as possible. The temperature was set at 12.5°C one night; the following morning it was still 12.5°C, and the mercury level had dropped to a point corresponding to curve B. Points on this second curve were obtained from 12.5 down to o°C, and back up to the melting point, but it was not possible to duplicate this curve.

A smooth curve (B) could be plotted from the melting-point down to 0°C and from 0-12°C and rechecked with good results, but from 12°C to the melting point, consistent readings could not be obtained.

It should be emphasized that this particular sample had obviously become contaminated. It was somewhat yellow in color, gave a melting point at least 2 degrees too low, and was only used because at the time no other speciman was available. Nevertheless, values for the density in the liquid state are in good agreement with values obtained by exact measurement. For instance, Deanesley[5] gives the density of hexadecane at 20°C as 0.77335, and our value was 0.7736.

Evidently sufficient impurity to alter the melting point by several degrees is not sufficient to cause any marked change in the density.

A second sample of hexadecane, obtained from the Shell Oil Development Company was investigated, and was found to have a melting point of 18.3°C and a setting point of 16.6°C. At the time of writing the density calculations for this sample have not been made, but a rough calculation places the density of the solid phase (for which only one curve was obtained) in the neighborhood of A rather than B.

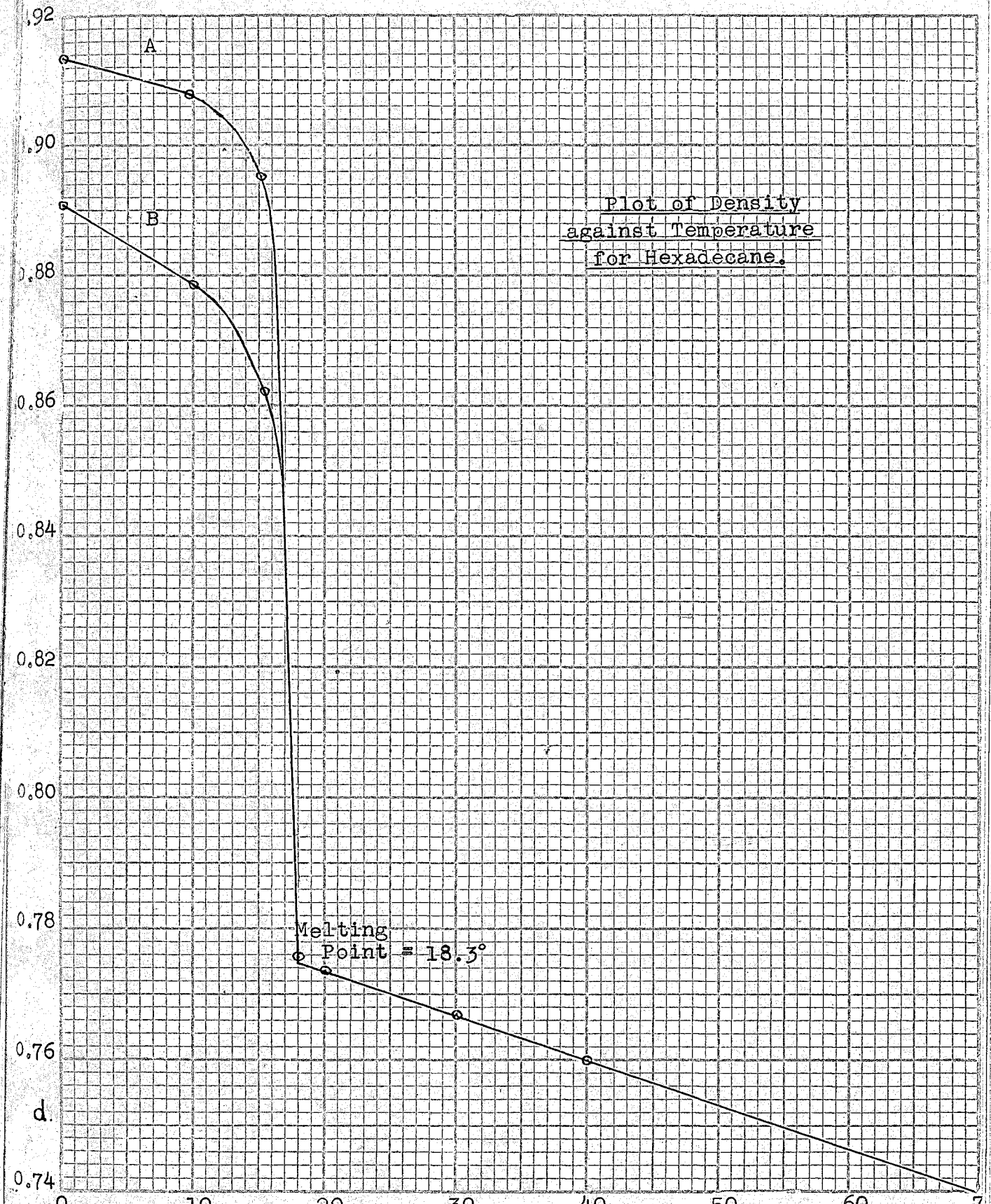


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FIGURE X

Eicosane:

With the even-numbered paraffins below 26, in the solid state, they assume the B form, with a spacing between that of the C and A form, according to Müller. It does not appear evident on theoretical grounds that these 001 spacings can be taken as a direct measurement of the densities; that is, as evidence to prove that the density measurements are a direct function of these spacings. Qualitatively, it is indicated. If the assumption is true, then the values of the densities for 20, 22, 24, in those regions close to the transition temperature should fall somewhere between the densities in the A form and those of the C form.

n.	(1) Density 2°C below trans.	n.	(2) Density 2° below trans.
		30	0.876
		32	0.873
		34	0.879
16	0.899		
20	0.909		
22	0.906		

n.	(3) Density 2° below trans.
30	0.924
32	0.923
34	0.923

Table XVII

(1) will correspond to the B form, (2) to the A form, and (3) to the C form.

The correlation appears good for these members, but in the case of 24, the B form is actually higher than that for the C form, rather than lower. If the above assumption were correct, namely, that the A, B, and C crystalline forms were a function of the sections of the density curves, then the solid region for 26, 28, 32 and 34 should lie in one region, those for 18, 20, 22, and 24 in another, and the transition points for 26, 28, 32, 34, in still another. Whether this is so, or whether the density for all even members of the series from 16 to 34 at 0°C should show a proportional increase with increase in chain length, is not certain.

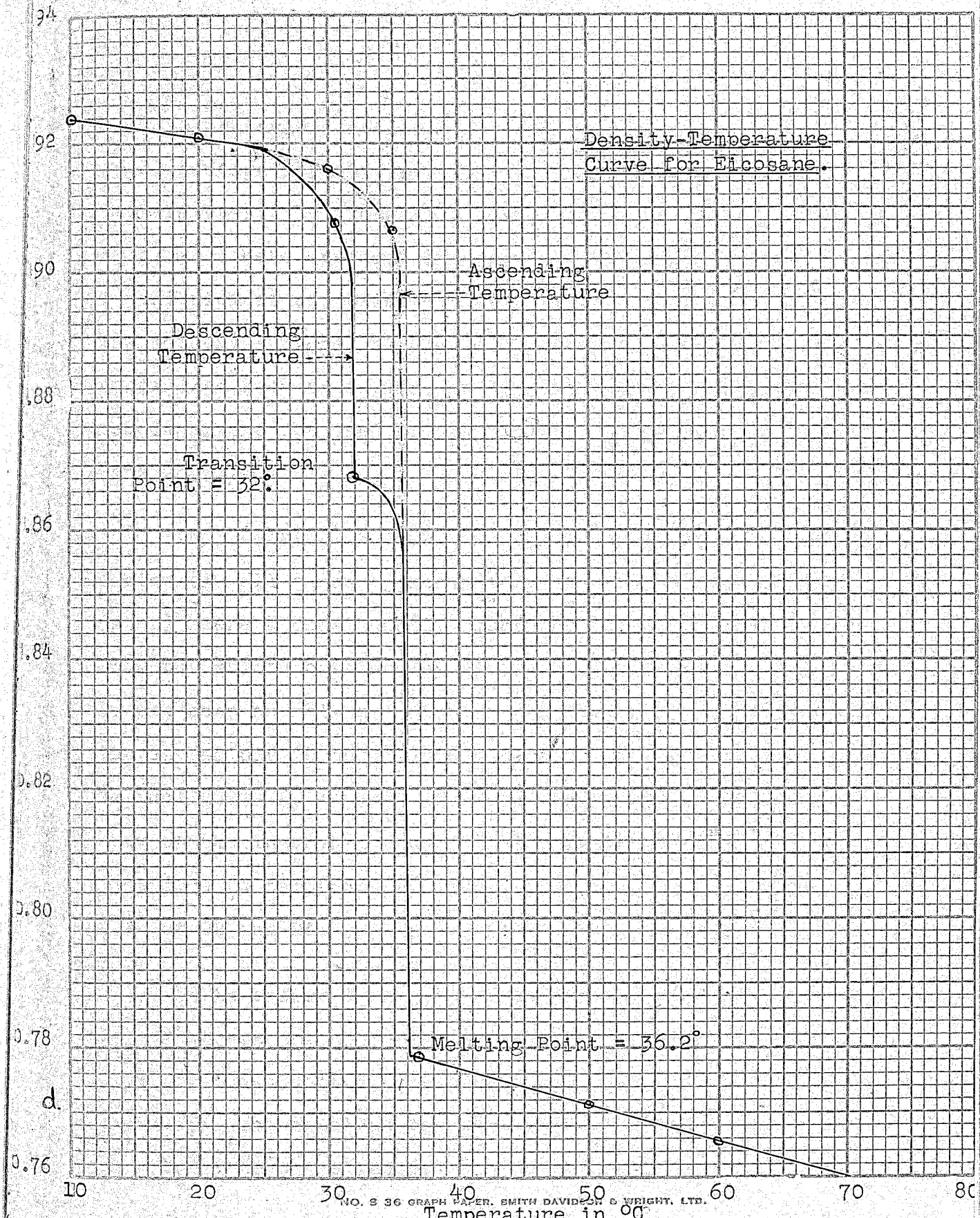
Density-Temperature Curve for Eicosane.
Ascending Temperature
Descending Temperature
Transition Point = 32°
Melting Point = 36.2°
.94
.92
.90
.88
.86
.84
.82
.80
.78
.76
d.
10
20
30
40
50
60
70
80
Temperature in °C.

FIGURE XI

Docosane:

Considerable difficulty was encountered in obtaining good readings for this sample, particularly for ascending temperatures. No transition was obtained on rising temperature, and there appeared a tendency towards disturbance of equilibrium at approximately 10°C below the melting point. The mercury surface, as viewed through the cathatometer telescope, was seen to quiver, and in this temperature region readings were obtained at distances considerably below the line shown.

In 3 samples, 20, 22, and particularly 26, there was a region (in all cases approximately 10°C below the melting point) where a consistently smooth curve could not be drawn from the points obtained on rising temperature. As mentioned in the note on melting points, certain sections of the density curves, mainly in the liquid region, could, with any one sample be duplicated any number of times within the limit of accuracy of the instruments used. All transition regions are sensitive to temperature change, and particularly so in the case of 22 and 26.

It is believed that the points lying on these sections of the curves are not reliable. The parts of the curve so considered are dotted, although the density values have been included. The sections in heavy lines are reproducible and considered to be reliable. The dotted regions will bear

further investigation, employing a more rigorous method of temperature control over a longer period of time.

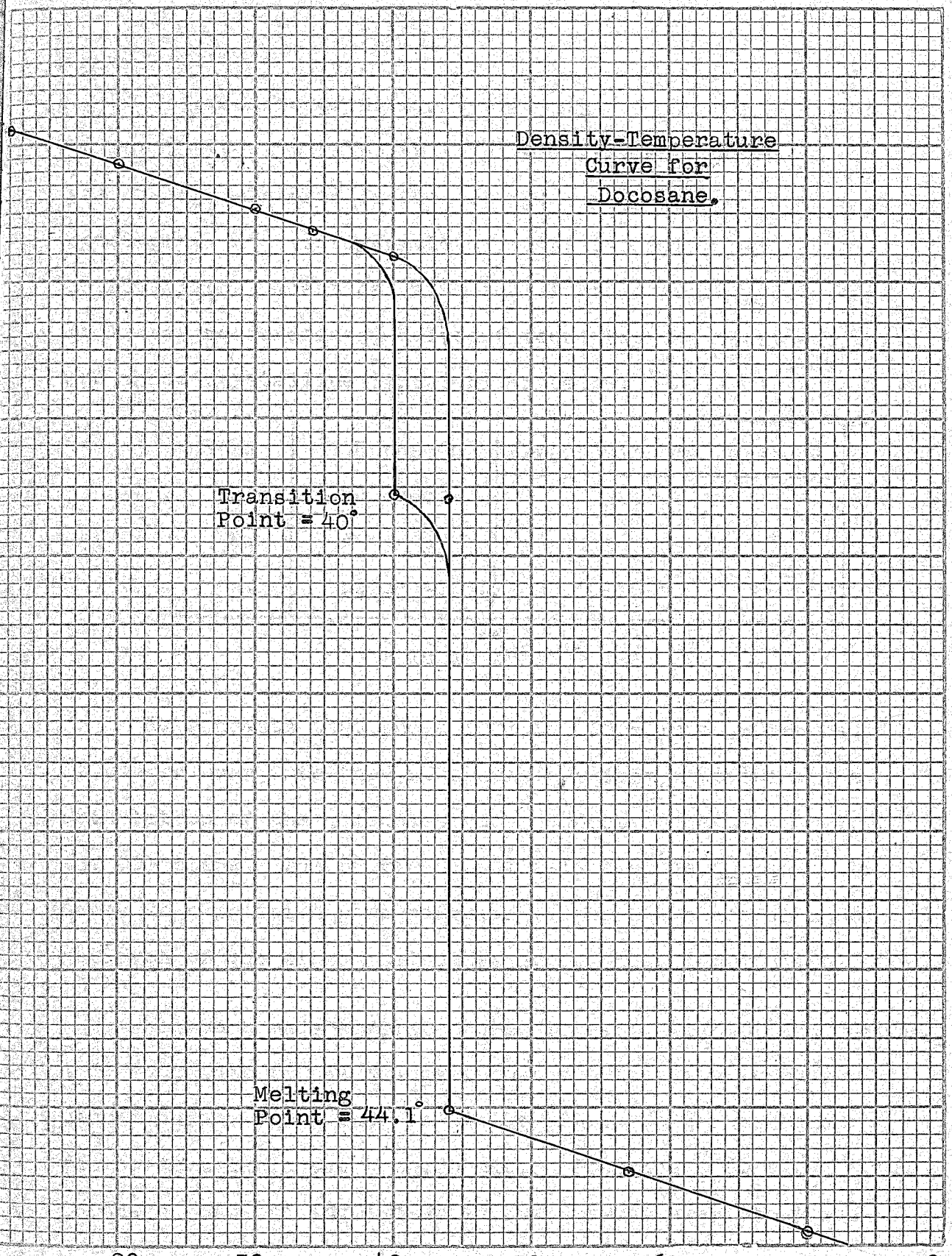

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FIGURE XII.

Tetracosane:

Before discussing the curve obtained for 24, it might be pertinent at this point to give a resumé of a recent article by Kolvoort[9] on the crystalline structure of this homologue. He used a sample of setting-point equal to 50.8, a value almost identical with that found in this laboratory. By ex-ray measurements, Kolvoort found two transition points and three crystalline forms, given below.

Form	Range	Transition Temperature
a.	50.8-46°	50.8°
b.	46° -41	46°
c.	below 41	41

Table XVIII

He suggests that the c form is monoclinic. Upon heating it passes over into the orthorhombic b form, retaining the orientation of the molecules with respect to each other in the 001 plane. The originally tilted molecule in the c form takes up a position perpendicular to the 001 plane with no rotation of the zigzag molecules above their longitudinal axes.

Kolvoort made a dilatometric investigation of the sample, and found that in the change from the c to the b form, a marked change took place in the density. No density change was observable in the transformation from the c to the a form. In the c form the angle between the optical axes decreases

within 0.3 degrees by 20% of its former value. In the b form the axial angle greatly depends on the temperature up to the point of transition from the b to the a form at 46, at which point the figure for uniaxial crystals is formed. Up to the melting point, the crystal remains uniaxial.

Müller notes that a change takes place first with 24. The a and b axes alter their length as the temperature increases, just as they did in the case of 20 and 22, but when a certain temperature has been reached (corresponding to the transition point), there is a sudden change in structure. The temperature of this transition is given as 40-41. Assuming that this value is the transition point, we have the three following values:

Transition Point.	Source..
41	Kolvoort[9]
40-41	Müller[13]
47.9	This Lab.

Table XIX

There is no apparent explanation for this wide variation. Kolvoort obtained one value of 36°C for this transition point, from a sample known to be impure. It is possible that the change in density takes place at the first transition, 45.8-46.4, which would be in fairly good agreement with our value. For comparison, 3 interpretations of the crystalline changes of octacosane are given in Figure XIV.

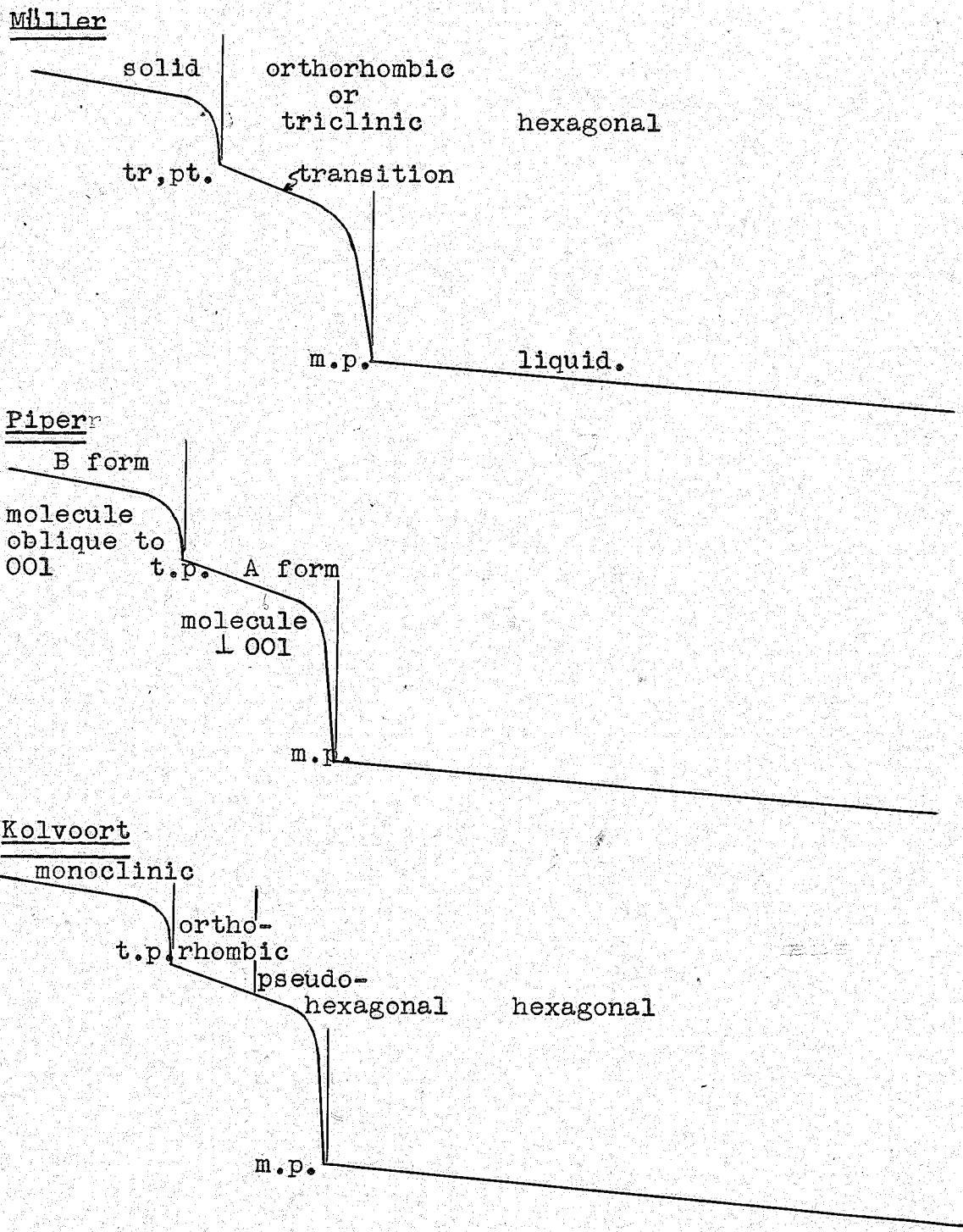

Müller
solid
orthorhombic
or
triclinic
hexagonal
tr.pt.
transition
m.p.
liquid.
Piper
B form
molecule
oblique to
001
t.p.
A form
molecule
⊥ 001
m.p.
Kolvoort
monoclinic
ortho-
t.p.
rhombic
pseudo-
hexagonal
hexagonal
m.p.

FIGURE XIV

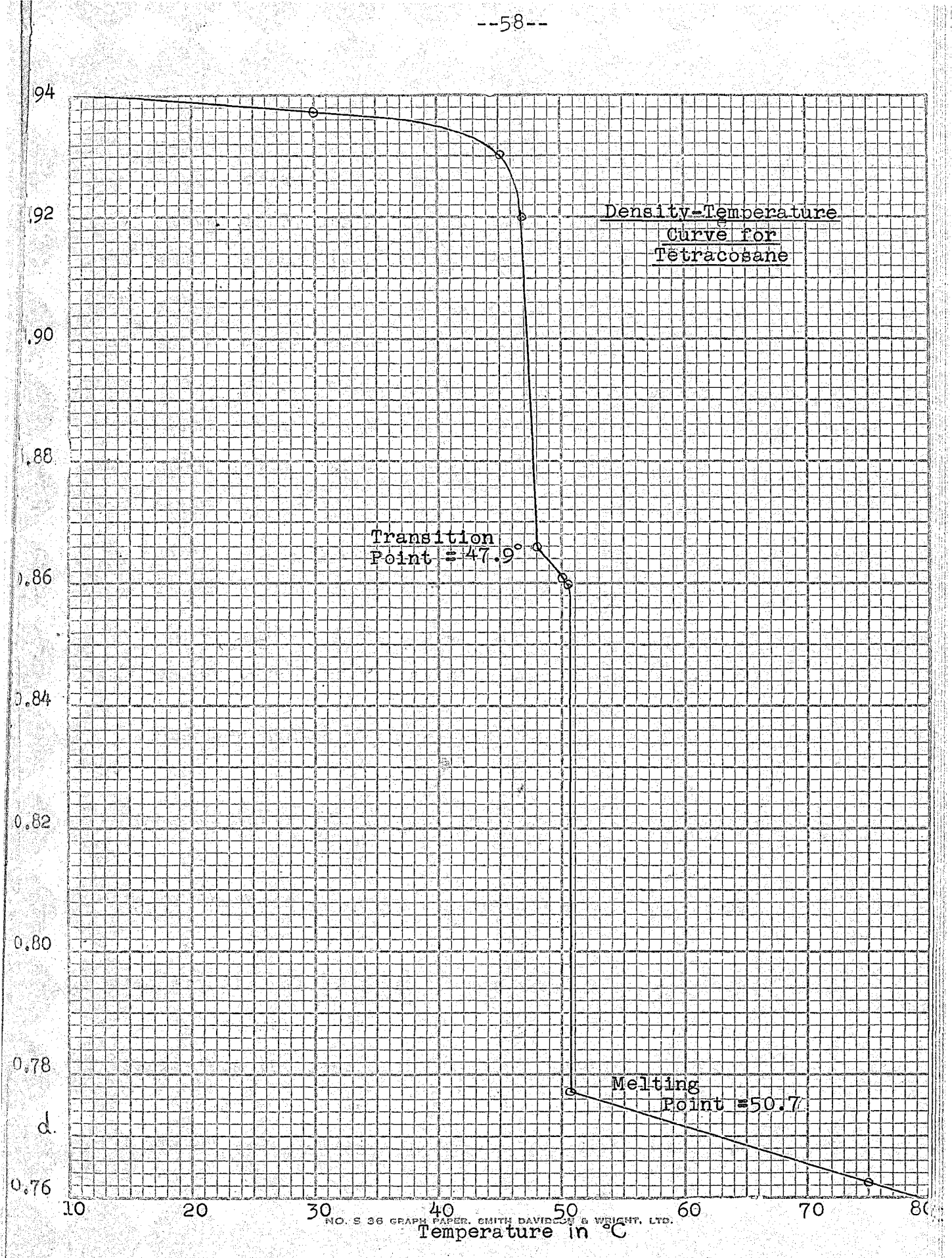

Density-Temperature
Curve for
Tetracosane
Transition
Point = 47.9°
Melting
Point = 50.7
94
92
.90
.88
.86
.84
0.82
0.80
0.78
d.
0.76
10
20
30
40
50
60
70
80
Temperature in °C

Figure XV

Hexacosane:

Two specimens of 26 were investigated. In the first case, shown in Figure XVII, the density calculations were not made. As seen from the capillary height-temperature curve, this specimen showed marked deviations from the usual curves. These can be no question as to the shape of the curves obtained. Section A-B-C of Figure XVII was repeated three times, and in one case, point A was held for 24 hours at 49.8±0.04°C on descending temperature scale. As before, the dotted part of the curve marks a region of uncertain readings. A region of instability was found to exist on rising temperature between D and E. The mercury had a tendency to oscillate, and in some cases two readings at the same temperature were widely divergent for consecutive runs.

Another sample was purified and investigated. The density curve is shown in Figure XVIII, and it is the least reliable of those obtained by the author. The readings were taken in a hurry, it being desired to obtain the general shape of the density curve for purposes of comparison. Again there was a region of instability and the same rise (to a much lesser extent) was observed at the transition point. No other member of the series showed this phenomenon. The first sample differed from the second in that the former showed no indication whatsoever of a sudden drop in capillary height at the transition point, whereas in the second case there was the usual drop, although the mercury dropped several cm below the

value shown on the curve, and then rose again.

As given in the general discussion on theory, 26 showed e-ray results differing from any other of the series. In a plot of spacing vs number of carbon atoms, given in Figure XVI, Piper, using his own values for 26,27 28,29,30, 31, 32, 34, 35, and 36, and those of Müller and Saville for 20, 22, and 24, shows that 26 has three spacings, in contrast to the other two well-marked series. Thus it might be expected that 26 would differ from the other members, but no explanation can be offered for the reasons why it should show such marked deviations from the adjacent members.

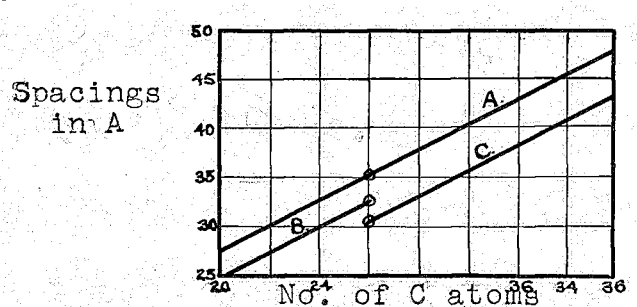


Figure XVI

Certainly with the apparatus used the temperature control was not sufficiently exact to obtain a smooth curve in the region of transition. With descending temperature, it was found impossible to obtain good readings from 40-56°C. In the first sample investigated, this region was carefully checked, the temperature being kept within this range for several weeks, and the region B-B' (Figure XVII) was checked every 0.2° each way for 15°C. The line was found to correspond in slope to similar lines found in the same region for other members. The straight

line obtained was reproducible within the degree of accuracy of the cathatometer, and the crystalline form was evidently a stable one.

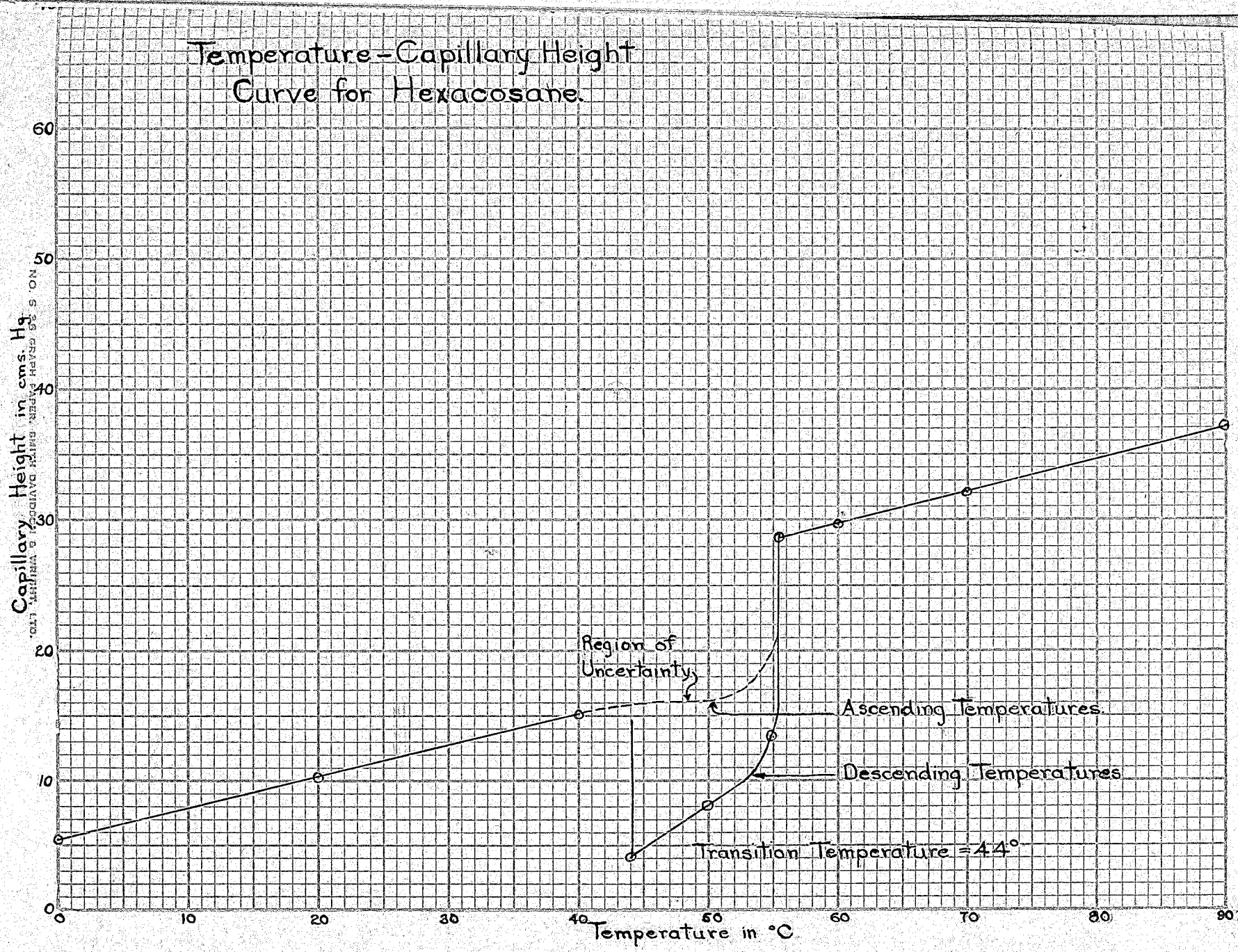

Temperature-Capillary Height
Curve for Hexacosane.
Capillary Height in cms. Hg.
0
10
20
30
40
50
60
Temperature in °C
0
10
20
30
40
50
60
70
80
90
Region of
Uncertainty
Ascending Temperatures.
Descending Temperatures
Transition Temperature = 44°

FIGURE XVII

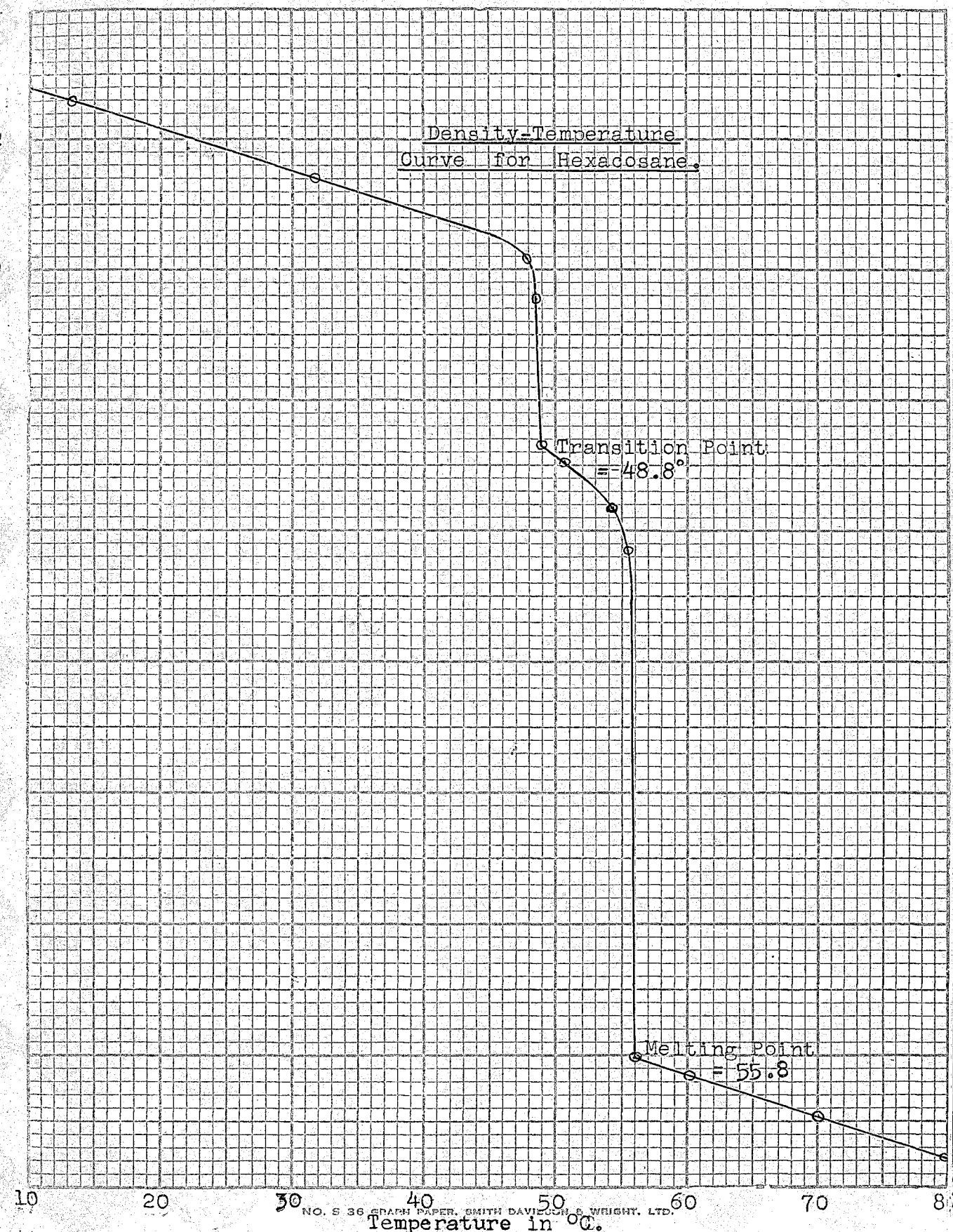


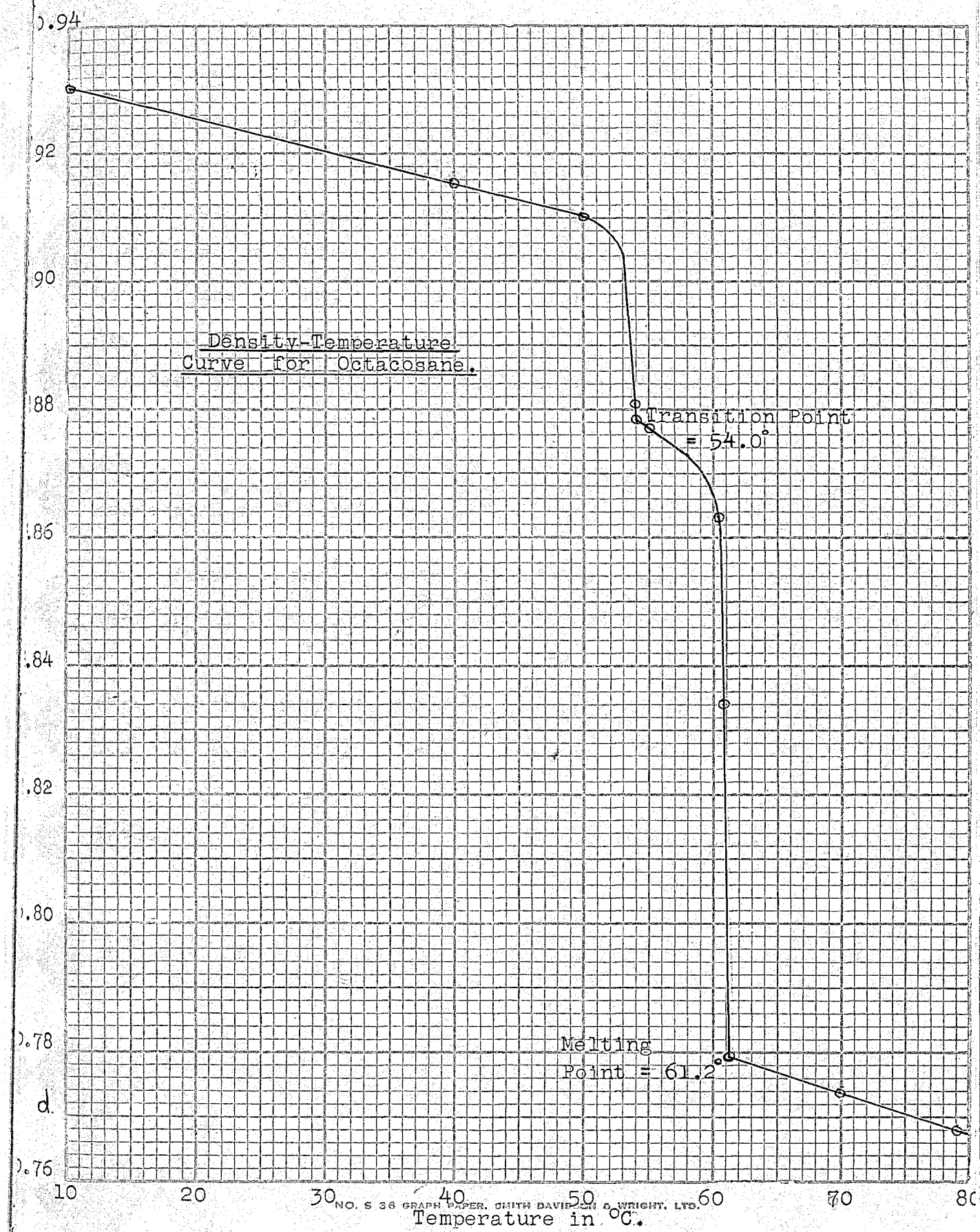
FIGURE XVIII

Octacosane:

The octacosane curve was regular with respect to transition and melting point. The heavy curve is the one assumed, but it is not the only one obtained. When the sample was first investigated, the temperature was raised to 85°C and the curve plotted on a descending temperature scale. The heavy line was obtained. On taking the temperature up from 0°C, the points checked until point A was reached. From then on a uniform divergence took place, and the same curve was traced on the way back. The entire curve was traced four times more, and of the six curves obtained, four followed A-B and two followed A-C, within the limit of measurement.

It is difficult to see what caused this divergence. It may be that in solidifying, minute voids are formed which the mercury does not fill completely. If this were true, then the mercury would not drop far enough, the capillary-height readings would be too high, and the density would be too low.

In that case, however, it would seem likely that the entire curve would be displaced vertically, rather than with the constant deviation actually obtained.



Density-Temperature
Curve for Octacosane.
Transition Point
= 54.0°
Melting
Point = 61.2°
d.
.94
.92
.90
.88
.86
.84
.82
.80
.78
.76
10
20
30
40
50
60
70
80
NO. S 38 GRAPH PAPER. SMITH DAVIDSON & WRIGHT, LTD.
Temperature in °C.

FIGURE XIX

Nonacosane:

Müller attributes at least three crystalline forms to 29: orthorhombic, monoclinic, and triclinic, with a hexagonal arrangement in the transition region. As discussed elsewhere the odd members with 11 or more carbon atoms normally crystallize in the A form, and the first transition is not accompanied by a change in the 001 spacing. For the transition region has been postulated[20] a crystalline form having the same 001 spacings as the A form (in which the transition form normally crystallizes) but of different cross section. This form may correspond to Müller's type B with no molecular tilt.

From the foregoing it might be expected that the solid section for 29 would be in the same region as the transition forms for the even members. From the curve it can be seen that the transition is far less marked than for the even members, and by comparison with 28 and 30, included for comparison, the curve shows the same general shape as postulated.

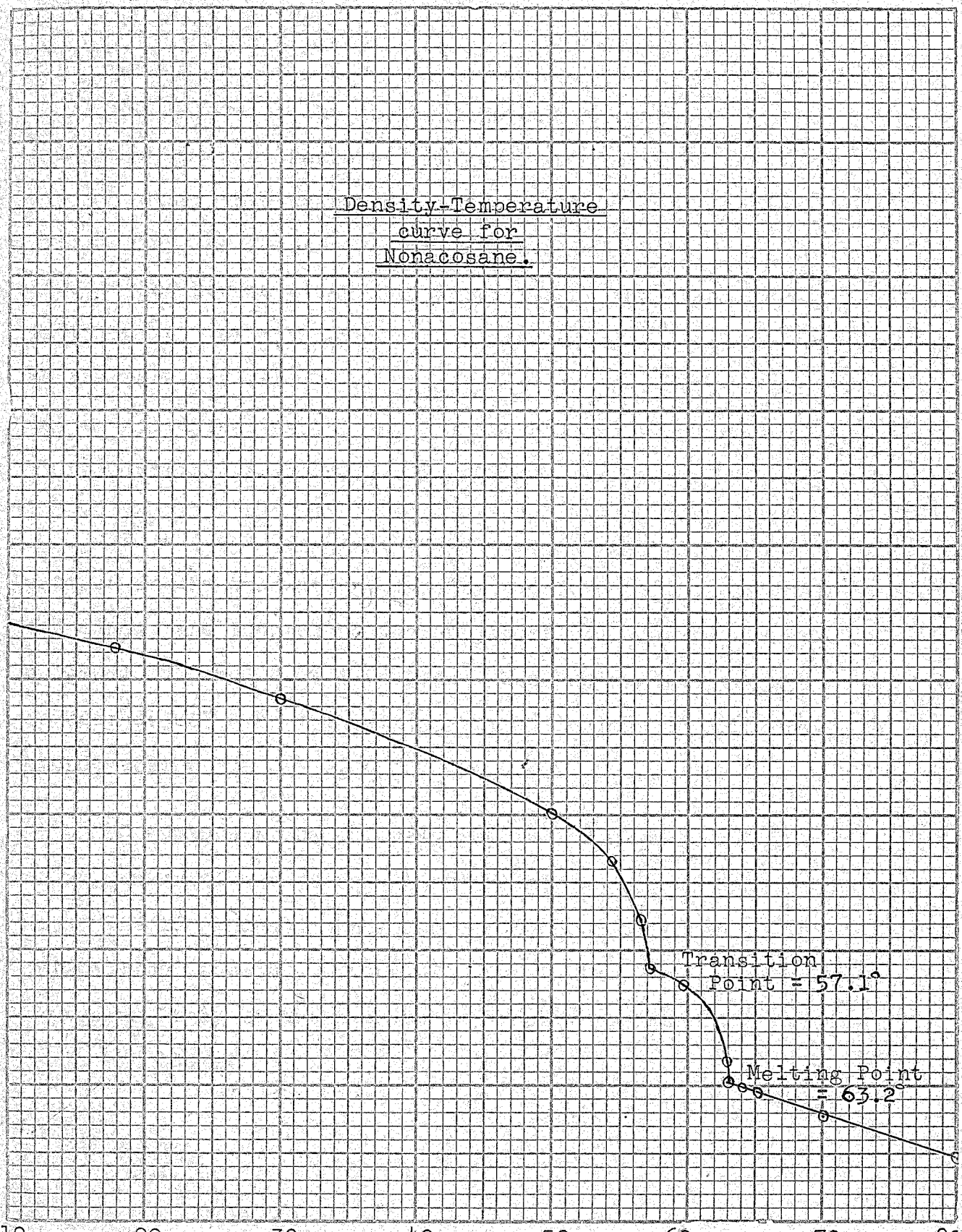

Density-Temperature
curve for
Nonacosane.
Transition
Point = 57.1°
Melting Point
= 63.2°
4
2
10
38
36
84
82
80
78
d.
76
10
20
30
40
50
60
70
80
Temperature in °C

FIGURE XX.

Triacontane:

The C form is the crystalline configuration in the solid state for the even members. Müller[13] mentions that the C form is only observable when the crystals are obtained from a solvent except when the members are in the neighborhood of 30. It is hard to see how this can be interpreted in the light of the fact that all of the members investigated by the dilatometer method show practically parallel lines in the solid state. It may be noted that in this work the samples must of necessity be crystallized from the liquid state.

In 30 there are 2 lines formed in the x-ray diffusion pattern in the transition region, one close to the original 110 lines, and the second weaker, about half way between the original 110 and 200 reflections. The angle ϕ (cf. p.43) approaches 60° near the melting point, indicating hexagonal close packing for the liquid range.

30 appears to be entirely regular as regards melting point, transition temperature and range, and lower solid and upper liquid ranges, so whatever changes or differences in crystalline structure may result from the above spacing relationships, they do not show up in density variations of measurable magnitude.

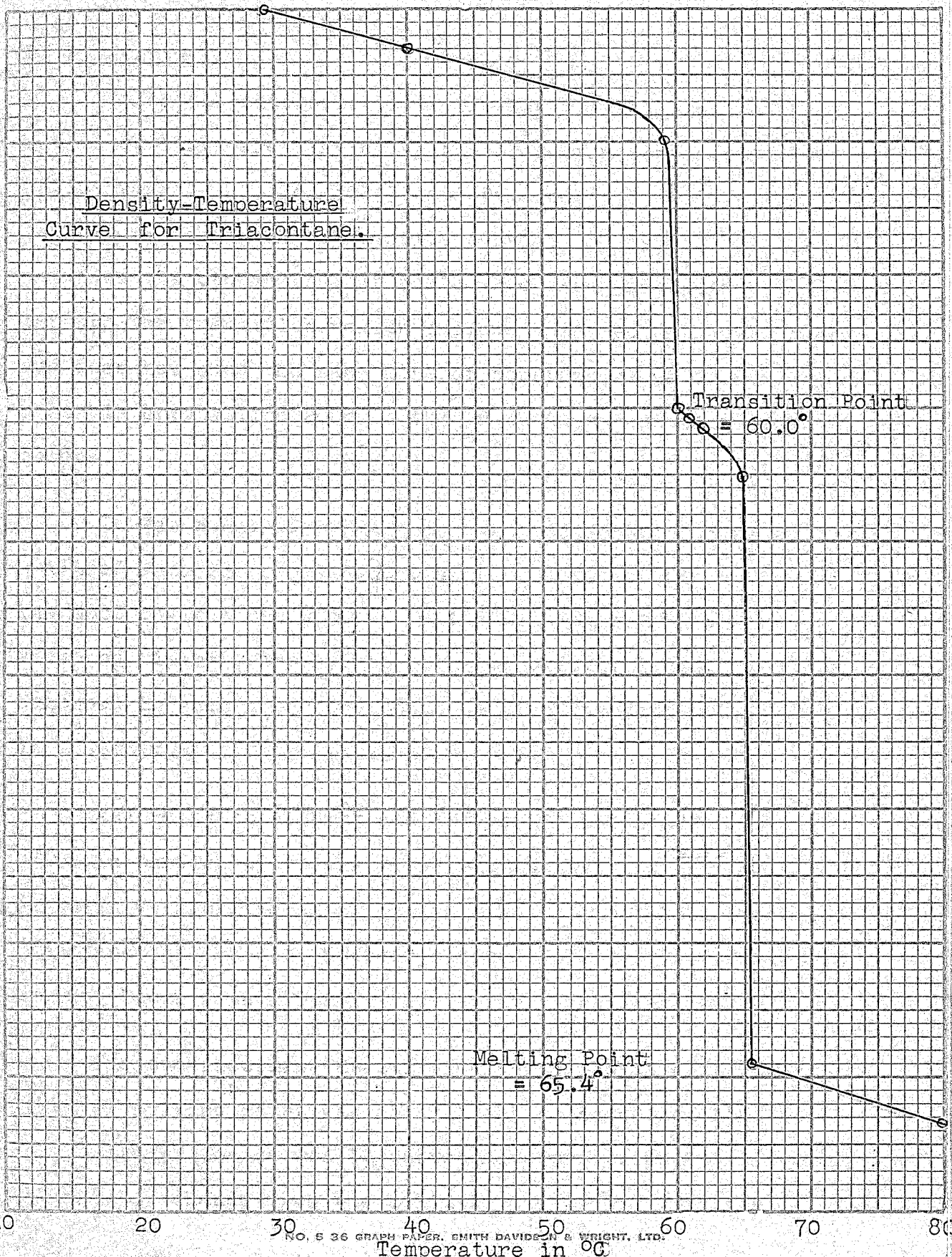

Density-Temperature
Curve for Triacontane.
Transition Point
= 60.0°
Melting Point
= 65.4°
10
20
30
40
50
60
70
80
Temperature in °C

FIGURE XXI

Dotriacontane:

Three separate samples of 32 were investigated. The three curves obtained are very close to one another throughout the entire range. 26, 28, 30, 32 and 34 show good correlation in the relationship between density curves. 32 is somewhat different from the others in that the change from one state to another through the transition region follows a perfectly regular curve and does not show the same line of constant slope (indicating a stable crystalline form in the transition region) as do the others.

It was wondered whether or not the density curves could be utilized as a means of indicating the purity of the specimen. The most obvious check would be the melting point, but as shown by Piper[22], two hydrocarbons of unequal length could be combined in such a proportion as to give the same melting point as a homologue lying between them.

According to Piper[22] and Kolvoort[9], the lower transition point is particularly sensitive to impurity, and therefore might be taken as a criterion of purity. This is of little practical importance at present, however, as the lower transition points are not known with a sufficient degree of reliability.

The one specimen investigated which showed a marked depression of melting point was 16. It may be seen from Figures X and XXII that the 16 and 32 curves have one property in common in that the change from the solid to the liquid form for 16, and

the change from liquid to transition forms in 32, show a broad curved section. The reason in each case may be the same; namely, the presence of impurity. On the other hand, in the light of the fact that 3 similar curves were obtained for 30, it may be that 32 shows this irregularity because of intermolecular forces peculiar to its chain length. The change from liquid to solid state without transition was extremely sharp in the case of the pure sample of 16; on the basis of this evidence it would appear as though some constant impurity were present in all three samples of 32 examined

Tetratriacontane:

34, the density curve for which is shown in Figure XXIII, appeared normal in every respect.

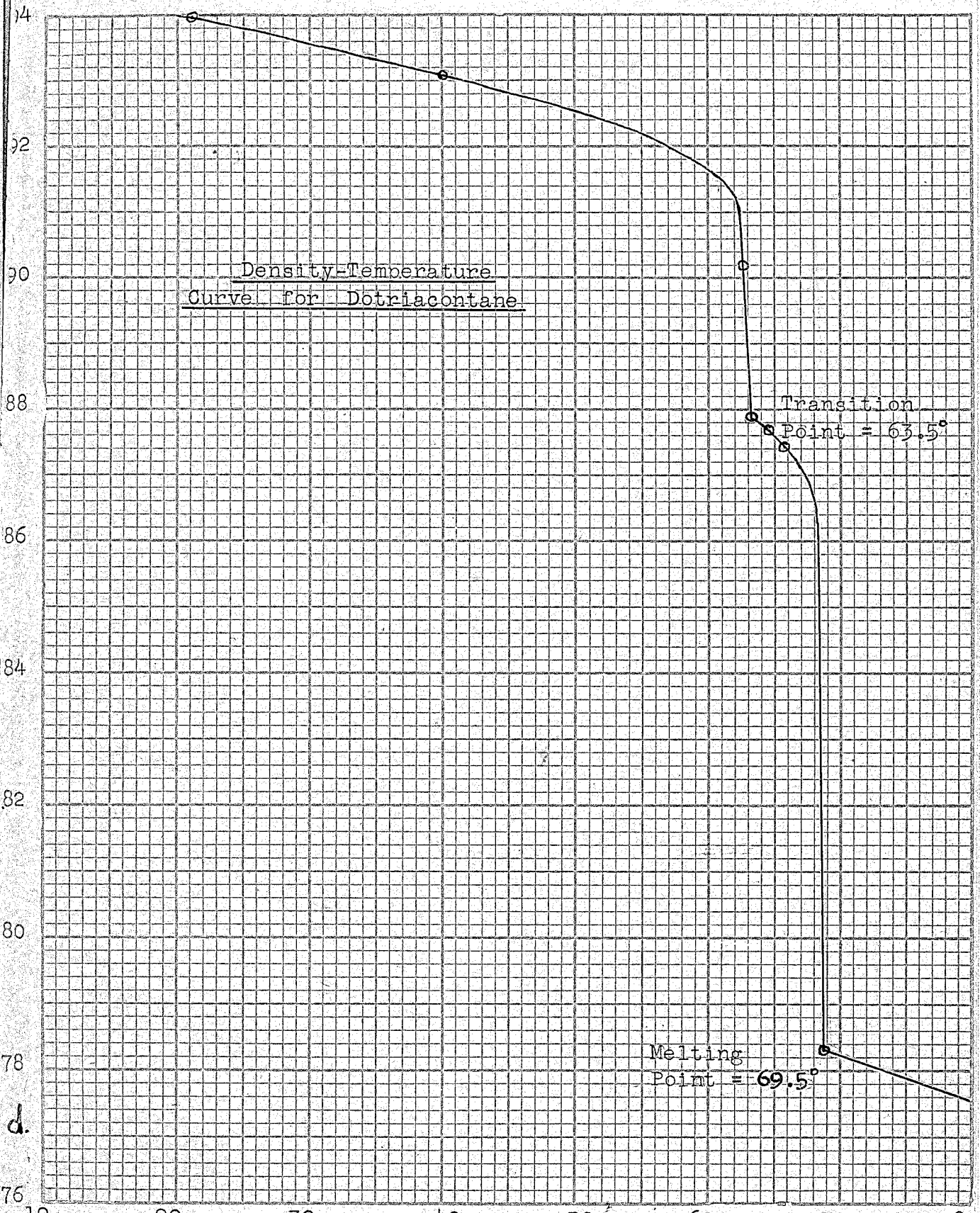

Density-Temperature
Curve for Dotriacontane.
Transition
Point = 63.5°
Melting
Point = 69.5°
.94
.92
.90
.88
.86
.84
.82
.80
.78
.76
d.
10
20
30
40
50
60
70
80
Temperature in °C.

FIGURE XXII.

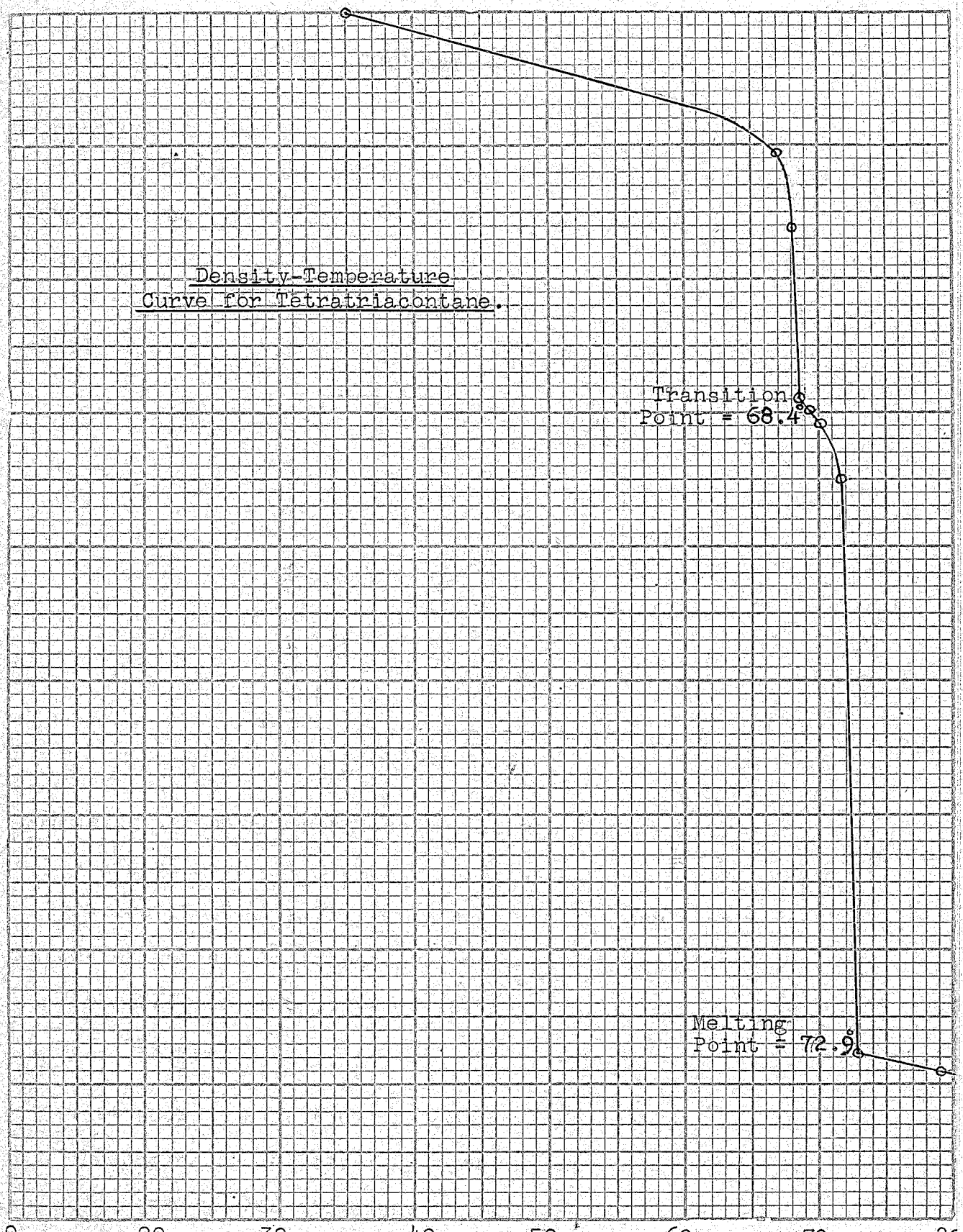


FIGURE XXIII

CORRELATION OF RESULTS

Transition Points:

The temperature of the second transition point (obtained upon cooling) is given in Table XX. Included with these experimentally determined temperatures is the single value for 44. According to Müller[16], the transition point becomes indistinguishable from the melting point for 44. Assuming this to be true,

n	Transition Point
16	None
18	
20	32
22	40
24	47.9
26	48.8
28	54.0
29	57.1
30	60.0
32	63.5
34	68.4
44	84.8

Table XX

and using our selected valuesfor the melting point of 44, (cf p..) its value istaken as the transition point of 44. These values are plotted in Figure XXIV. From the curve obtained, values of the second transition point have been selected and in Table XXI they are compared with transition temperatures given by Piper.

24 shows the greatest deviation from a smooth curve. In the discussion on 24 (cf. p.55.) it was pointed out that this member showed marked differences in several respects.

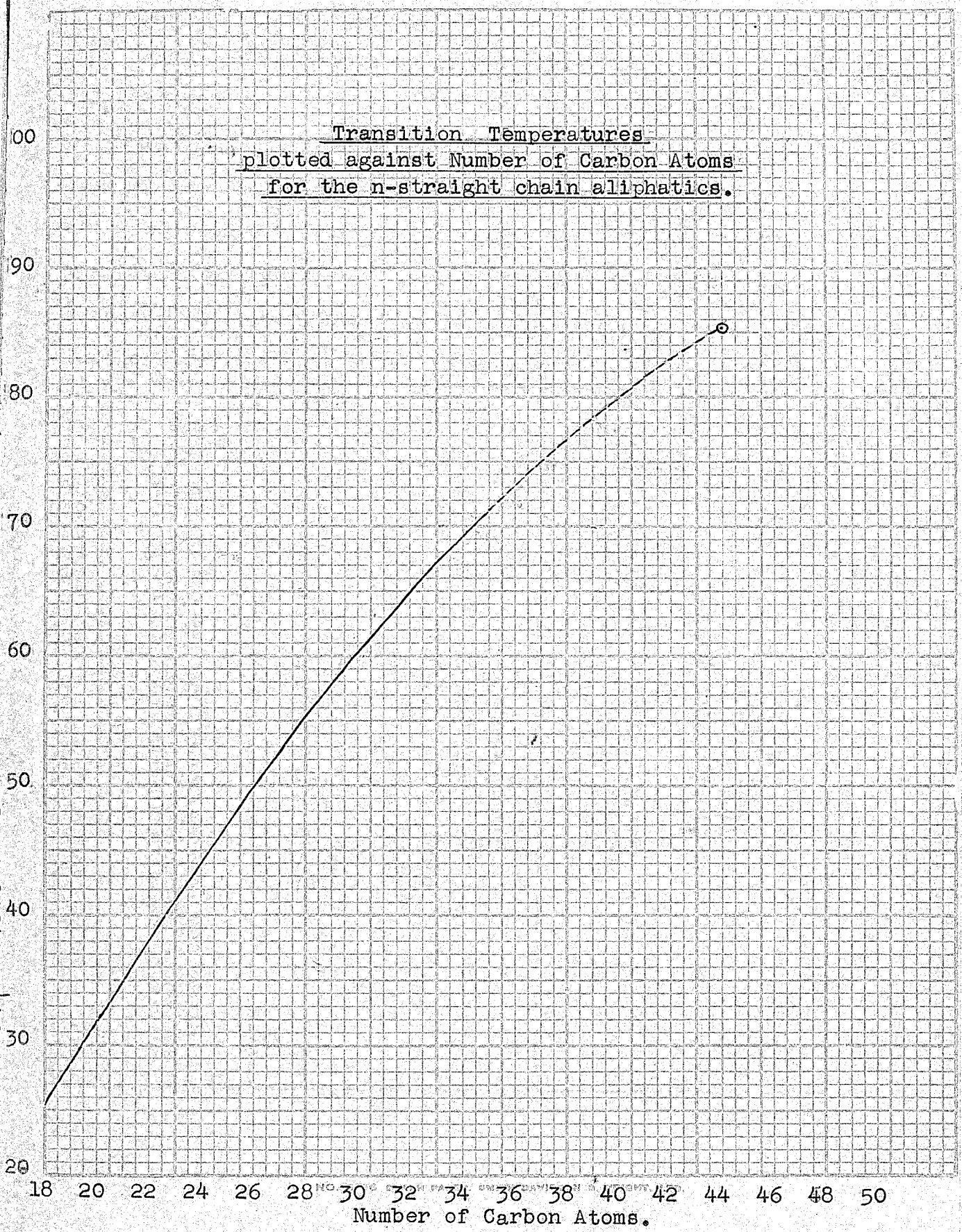

Transition Temperatures
plotted against Number of Carbon Atoms
for the n-straight chain aliphatics.
100
90
80
70
60
50
40
30
20
Temperature in °C.
18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50
Number of Carbon Atoms.

FIGURE XXIV

It is not possible to give a close comparison of the selected values and those of Piper. The transition points obtained from the temperature-density curves are obtained in exactly the same manner as the setting point, and they can be measured with any degree of fineness desired (cf. p.18), whereas Piper records two sets of values, one resulting from a descending, the other from an ascending temperature, and furthermore, they are given in a range.

n.	Selected Trans pt.	Piper's Values for Trans Point Cooling.	Heating.	Observed Trans pt.	Diff.
18	26.0				
19	29.7				
20	33.2			32.0°C	-1.2°C
21	36.3				
22	40.0			40.0	-0.0
23	42.2				
24	45.0			47.9	2.9
25	47.8				
26	50.2	48.3	51.5-52.0	48.8	-0.4
27	52.9	51.0	52.8-53.0		
28	55.2	54	57.0-57.5	54.0	-1.2
29	57.5	55.8	57.3-57.5	57.1	-0.4
30	60.0	58.0	59.0-59.5	60.0	0.0
31	62.3	61.8	62.0-62.5		
32	64.5	63.9	65.2-65.4	63.5	-1.0
33	66.8				
34	68.6	68.5	69.2-69.4	68.4	-0.2
35	70.4	70.5	71.8-72.0		
36	72.8	72.5	73.9-74.1		
37	74.2				
38	76.0				
39	77.6				
40	79.1				
41	80.8				
42	82.0				
43	83.4				
44	84.8				
45					

Table XXI

The transition point can approach the melting point in either one or both of two ways. The temperatures can converge, or the density of the transition state can approach that of the solid state. In Table XXII is recorded the density of the hydrocarbons investigated at the transition point, together with the transition temperature, the setting point temperature, and the difference between them.

In Figure XXV is shown a plot of t vs n. The points are too scattered to warrant drawing a curve through them, although there does seem a tendency for difference between the trantision temperature and melting point to approach 0 at n = 44.

If the densities of the A and C forms (cf. p.39) approach each other at 44, then (from Figure XXVI), the density of 44 in the solid state should be approximately 0.898. In Figure X is shown an extrapolation of solid form densities (based on an assumption that the solid phase density curve for 44 will be only slightly above that of 34) down to the melting point of 44. The density of 44 according to this extrapolation would be 0.917 compared to the 0.898 from Figure XXVI.

From Figure X it would appear that the latter figure is too low, and that the predominating effect with increasing chain length is a diminishing transition range.

n	Density at t.p.	Temp. of t.p.	m.p.	t.
18				
20	0.8670	32.0	36.2	4.2
22	0.8690	40.0	44.1	4.1
24	0.8673	47.9	50.7	2.6
26	0.8722	48.8	55.8	7.0
28	0.8788	54.0	61.2	7.2
30	0.8802	60.0	65.4	5.4
32	0.8782	63.5	69.5	6.0
34	0.8836	68.4	72.9	4.5
29		57.1*	63.3	6.2
31		61.8*	68.0	6.2
35		70.5*	74.4	3.9

* Values taken from Piper.

Table XXII

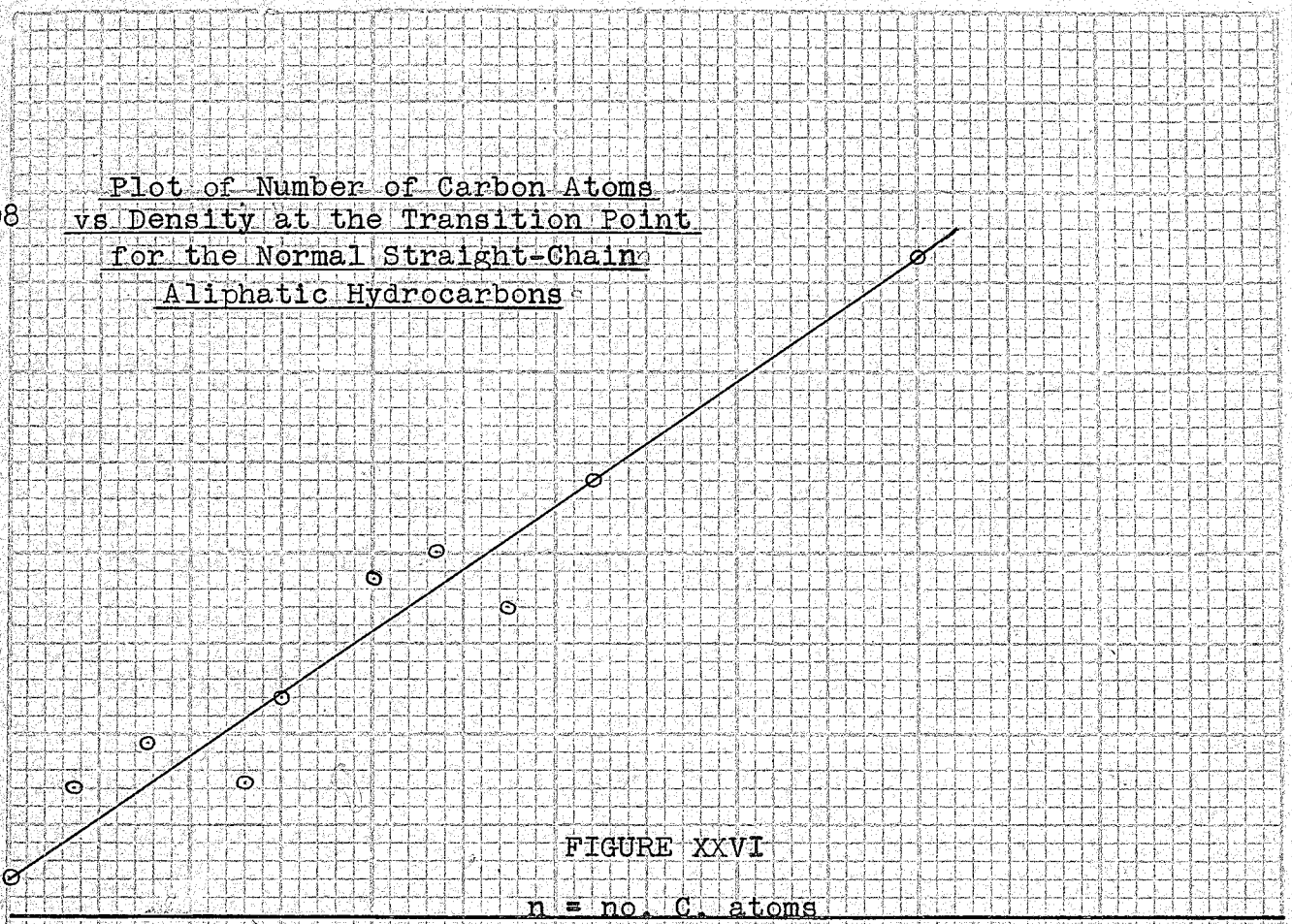


FIGURE XXVI

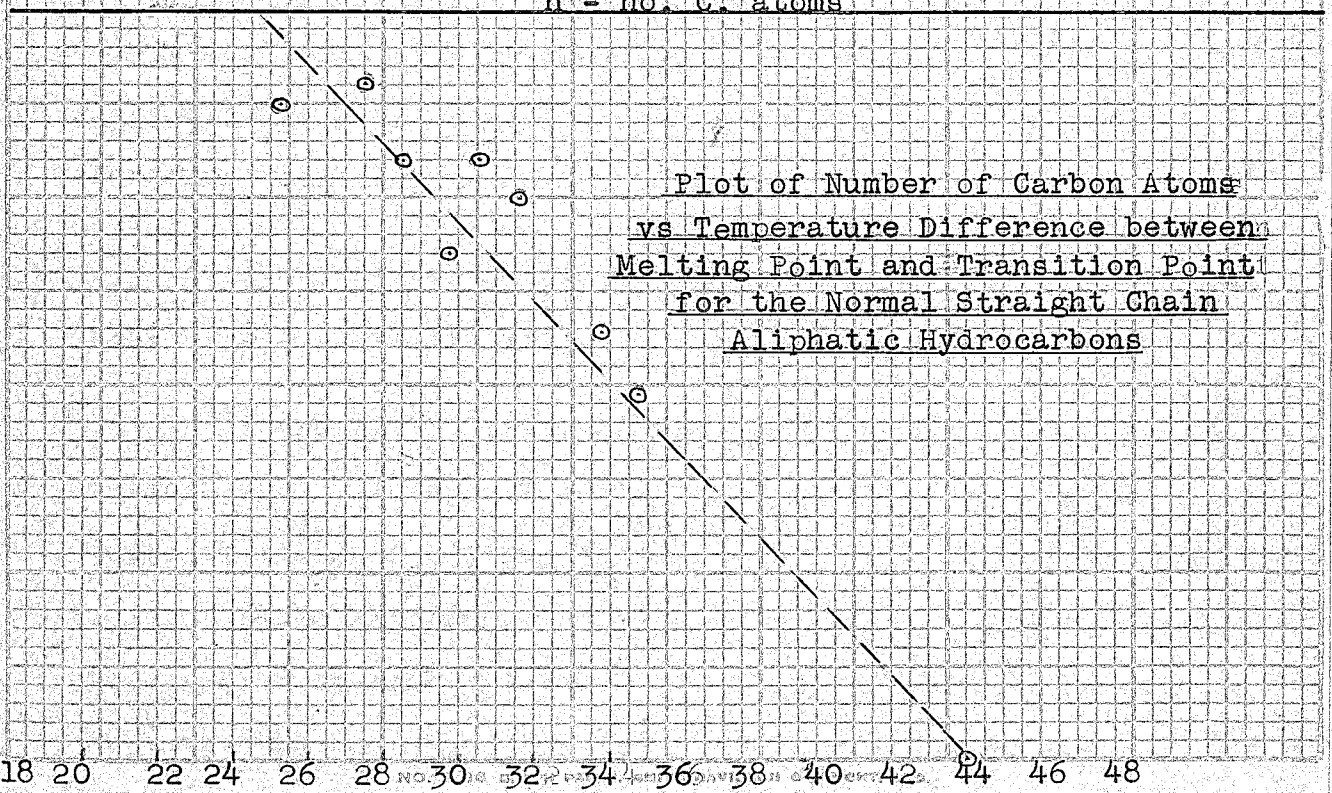


FIGURE XXV

Shapes of Curves Over Entire Temperature Range:

The question arises as to the shape of the density curves over the entire temperature range from 0-500°Abs, that is from absolute zero to well above the boiling point. Since the coefficient of expansion of a crystalline substance becomes zero at 0°Abs, it is probable that the density approaches some value close to 1.0 at very low temperatures. The densities of the long-chain members have not been measured at higher temperatures, but it was thought possible to obtain some knowledge of these regions from data already obtained for the lower members.

If we assume that the liquid lines for all hydrocarbons are parallel and of the same general shape throughout, then the slope of all members at any given temperature interval between boiling-point and melting-point (say, half-way between) should be approximately the same. The data given in Table XXIII is taken from Deanesley.

The temperature interval between boiling point and freezing point for 26 is 366.4-55, or 311°C.

In Figure XXVII, this interval is divided into decimal fractions, and values of the coefficient of expansion at fractional distances within this interval (taken from the last column of Table XXIII are plotted. The value of $d(d)/dt$ at the boiling point we know. (It is essentially infinity.) We also know that $d^2(d)/dt^2$ is 0 for the 15-20°C range above the

n	d(d)/dt	b.p. at 760 mm.	f.p. at 760 mm.	t, bp to fp	t, 20° to mp.	Fraction of 20°C betn. bp and fp.
5	0.000975	36.1	-129.7	165.8	149.7	0.962
6	0.000891	68.7	- 95.3	164.0	115.3	0.704
7	0.000840	98.4	- 90.6	189.0	110.6	0.584
8	0.000803	125.6	- 56.8	182.4	76.8	0.421
9	0.000774	150.7	- 53.7	204.4	73.7	0.360
10	0.000751	174.0	- 29.7	203.7	49.7	0.244
11	0.000733	195.8	- 25.6	221.4	45.6	0.2062
12	0.000719	216.2	- 9.60	225.8	29.6	0.131
13	0.000708	235.5	- 6.00	241.5	26.0	0.108
14	0.000699	253.6	5.5	248.1	14.5	0.058
15	0.000692	270.6	10.0	260.6	10.	0.042
16	0.000686	286.5	18.1	268.4	2.	0.007

Table XXIII

melting point (deduced from the line of constant density change obtained in the case of each hydrocarbon investigated.) Table XXIV gives the values of d(d)/dt immediately above the melting point for the even members.

n	d(d)/dt
18	
20	0.000634
24	0.000632
26	0.000622
28	0.000668
30	0.000628
32	0.000641
34	0.000620
Average	0.000636

Table XIV

Therefore the curve in Figure XXVII should be asymptotic to d(d)/dt = 0.000636 at the lower boundary limit. Actually the lower limiting value of d(d)/dt from the curve is 0.00068 to 0.00069. It is not plain why the calculated value of d(d)/dt

at the melting point should be so much higher than the observed value.

Despite the unsatisfactory quantitative relationship shown in Figure XXVII, however, it does indicate that there is probably no marked increase in the slope of the density curve as the temperature approaches the boiling point, and that the sharp decrease in density at the boiling point takes place within a small range, say less than 5°C..

SUMMARY.

1. Melting Point values for the entire n-paraffin hydrocarbons have been compared and a table of tentative values arranged.

2. Density curves for 16,20,22,26, and 34 have been obtained.

3. The above curves, together with those for 24,28,29,30, and 32 have been discussed in terms of crystalline structure in the liquid, transition and solid states.

4. Transition points of all members from 16 to 44 of the even series have been correlated, and the approach of melting point and transition point with increasing chain length discussed.

5. An attempt has been made to predict the shape of the density temperature curves for the even n-paraffin hydrocarbons of long carbon chain over the entire temperature range.

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APPENDIX I

PREPARATION AND PURIFICATION OF THE HYDROCARBONS

Tetradecane, Pentadecane, and Hexadecane:

These three members were obtained from Parks of the University of Stanford, and were part of the same materials used in heat of fusion measurements. 14 and 15 were considered to be of sufficient purity to be employed as received.

The sample of 16 was found to have a setting point of 15.9°C, at least 2.0°C below the accepted value (cf page 38), and it was deemed necessary to repeat the density determination. A 5-gram sample was obtained through the courtesy of the Shell Development Company, and was part of a specimen used by Deanesly and Carrothers[5] in density, melting-point, and refractive index measurements. This sample was considered to be of the highest possible purity, and in order to avoid any contamination, was transferred to a dilatometer bulb with as little exposure to airas possible, and without further treatment.

Octadecane:

18 was synthesized by the Peterson synthesis (cf page 89-90) from Kodak Capric acid. Acetic acid was used as a solvent, the crystallized needles being filtered off at a temperature just slightly above the freezing point of the acetic acid-hydrocarbon solution.

APPENDIX I (Continued)

Eicosane:

20 was synthesized from Decyl alcohol (Kodak) by the same method as that used for 24, 28, and 32, then purified from sulphuric acid, acetic acid, and ethyl alcohol. Due to the care taken in the synthesis and purification of 20, it was considered to be one of the purest members used. The Sorabji[37] modification of the Krafft[33] reaction is a general one, and the following equations are applicable in form to 24, 28, and 32.

1. $C_{10}H_{23}OH + HI \longrightarrow C_{10}H_{23}I + H_2O$
2. $2C_{10}H_{23}I + 2Na \longrightarrow 2NaI + C_{20}H_{42}$

Docosane:

22 was synthesized from Lauric acid (Kodak) by electrolysis. The method of preparation, taken from Peterson[21] is as follows:

a. Neutralize 15g. lauric acid by warming with approximately 5g. of K_2CO_3 plus 75cc of water.
b. Add together with 50cc of 96% ethyl alcohol and another 5g. of lauric acid.
c. Place solution in a 300cc beaker, and when the temperature has dropped to 45°C, pass a current of 0.84 amps C.D. between 2 platinum electrodes (If the electrodes are smooth, the surface area should be approximately 15cm^2.), holding the temperature between 45 and 50°C.

APPENDIX I (Continued)

d. Every two hours add 6g. of lauric acid dissolved in alcohol until 40g. of lauric acid have been added, the electrolysis proceeding for fifteen hours. The hydrocarbon collects on the surface as an oily liquid and can be removed as a solid upon cooling to room temperature.

e. Reflux with a solution of potassium carbonate or hydroxide in order to remove the decomposed lauric acid.

f. Boil with water, alternately cooling, pouring off the water, and adding fresh water and boiling until a clear solution is obtained.

g. Reflux with alcoholic potash in order to saponify completely any $C_{11}H_{23}COOC_{11}H_{23}$ formed.

The chief reactions in the Peterson synthesis are:

1. $2C_{11}H_{24}COOH \longrightarrow 2C_{11}H_{23}COO + H_2$

2. $2C_{11}H_{25}COO + H_2O \longrightarrow 2C_{11}H_{23}COOH + O$

3. $2C_{11}H_{23}COO \longrightarrow C_{22}H_{46} + 2CO_2$

4. $2C_{11}H_{23}COO \longrightarrow C_{11}H_{23}COOC_{11}H_{23}$

5. $C_{11}H_{23}COOH + CH_3CH_2OH \longrightarrow C_{11}H_{23}COOC_2H_5$

These reactions are quite general, and any of the radical used in obtaining other members of the series could be substituted for the $C_{11}H_{23}$ group.

APPENDIX I (Continued)

Docosane: (Continued)
Reaction 3 is the only one desired.

Reaction 4 is suppressed by the addition of potassium carbonate.

Peterson decided from the high saponific value of his product that approximately 4.4% of $C_{11}H_{23}COOC_{11}H_{23}$ and approximately 2.9% of $C_{11}H_{23}COOC_2H_5$ were formed during the electrolysis. They are removed by procedure 'f' above.

That reaction of equation (2) takes place to some extent was deduced from the highe current consumption.

The per cent yield is from 85 to 90.

The particular sample of 20 used was not treated with sulphuric acid, a fact which may account for the somewhat low melting point (cf page 21)

Tetracosane:
24 was synthesized from Eastman Kodak Company Lauryl alcohol, using the Krafft method (cf page 90). Of all the hydrocarbon members investigated, 24 gave the most marked deviations from homologous properties, and for this reason may be considered to be the most suspect as regards purity.

APPENDIX I (Continued)

Hexacosane:
26 was prepared in the same manner as 22, using myristic acid (Eastmann Kodak) under the following conditions: 15g. myristic acid plus 4½ g. potassium carbonate together with 75cc water plus 50cc 98% alcohol, using a current density of 0.96 amps at a temperature of 55-60°C. The per cent yield was 85-90

Octacosane:
28 was obtained from myristic acid (Kodak), by means of the Fittig Reaction:

a. 25g. of myristic acid is melted and hydrogen iodide is bubbled in, the HI being generated by the action of water (1 part) and I_2 (11 parts). The reaction is considered complete when all the material in the reaction flask remains liquid at room temperature. Tetradecyl iodide is formed.

b. The product is slowly poured into 200cc of dry ether containing a slight excess of the theoretical amount of Ns required for the reaction.

c. The mixture is refluxed for six hours.

d. The ether is evaporated off and the excess Na removed with 95% ethyl alcohol.

APPENDIX I (Continued)

Octacosane: (Continued)
e. The alcohol is evaporated off and the hydrocarbon formed is purified by treatment with sulphuric acid and acetic acid.

Nonacosane:
The sample of 29 used was obtained from the American Bureau of Standards. It was purified by repeated crystallization from glacial acetic acid and pure ether.

Triacontane or dicetyl:
30 was obtained by electrolytic synthesis, using as original charge 20 g. of palmitic acid (Kodak), 5 g. of KOH, 100cc of water, and 75cc of ethyl alcohol, maintaining a current density of 2.5 amps/square decimeter at 5 volts, at a temperature of 70°C. 3g. of palmitic acid, dissolved in hot alcohol, were added every two hours, and the product was purified by treatment with concentrated sulphuric acid and crystallization from glacial acetic acid.

Dotraicontane:
32 was synthesized from Cetyl alcohol (Kodak), by the same method as that [redacted] used for 20. It was purified in the usual manner. In this case 3 density-temperature curves were obtained[10], two from synthesized samples and one from a sample of the hydrocarbon obtained from the Eastman Kodak Company.

APPENDIX I (Continued)

Tetratriacontane:

The Peterson electrolytic method was used to synthesize 34. Using Kodak stearic acid, an recovery of 75-80% was obtained with a current density of 0.98 at a temperature of 75°C.

One sample obtained by this method was found impossible to obtained in a colorless state. It is possible that the reason lies in the following statement of Oldham and Ubbelohde[17]: "Owing to the appreciable oxidation of certain liquid paraffins at 130°C, it was advisable to hinder the circulation of air over the surface of the paraffin during the purification."

This we did not do, and it may be that repeated purification at temperatureswell over 100°C resulted in the formation of products of oxidation which contaminated the sample we were attempting to purify.

APPENDIX II

CALIBRATION OF HEXADECANE DILATOMETER TUBE

Mass of mercury.....76.1775g

Volume of mercury at 50°C..... 5.654115g

Volume of mercury at 30°C..... 5.633722g

Difference in volumes of mercury at

50°C and 30°C..... 0.020393

Correction for expansion of glass

= 30(5.633722)(0.0000096)..... 0.001366g

Net expansion of mercury..... 0.019311

Difference in mercury levels..... 3.120 cm.

A = cross-sectional area of tube

= 0.019311/3.120..... 0.006163 cm^2

(Average value of A found over range 0-80°C

range..... 0.006175cm^2

Volume of bulb to O-point at 30°C

$= V^{o}_{30} = V^{h}_{30} - hA$

= 5.633722-(24.87)(0.006175)

..... 5.48044 cc

APPENDIX II (Continued)

Calculation of density:

t = temperature at which reading was taken

h = height of mercury column above zero clip

A = cross-sectional area of capillary tube

V^{o}_{30} = volume of the bulb to zero-point at 30°C

V^{h}_{30} = total volume of mercury to height h at 30°C

$$= V^{o}_{30} - hA$$

V^{h}_{t} = total volume to height h at t°C

$$= V^{h}_{30} - V^{h}_{30}(t-30)(0.0000096),$$

where 0.0000096 is the coefficient of cubical expansion of glass, (Pyrex)

W = total mass of mercury in dilatometer with hydrocarbon

V_t = volume of mercury in dilatometer at t°C

or (W)(specific volume of mercury at t°C)

w = weight of the hydrocarbon in dilatometer bulb.

v_t = volume of hydrocarbon in bulb at t°C

$$= V^{h}_{t} - V_t$$

D_t = density of hydrocarbon at t°C = w/v_t

APPENDIX II (Continued)

Example: calculation of the density of hexadecane at 30°C

$t = 30°C$

$h = 26.55$ cm.

$A = 0.006175$ sq. cm.

$hA = (26.55)(0.006175) = \ldots\ldots\ldots\ldots\ldots\ldots 0.16381$

$V^{o}_{30} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5.48044$

$V^{h}_{30} = V^{o}_{30} - hA = 5.48044 - 0.16381 \ldots\ldots\ldots\ldots 5.64425$

$V^{h}_{t} = \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5.64425$

(Since there is no correction factor)

$W = 63.6800$ g.

$V_{t} = (0.0739552)(63.6800) \ldots\ldots\ldots\ldots\ldots\ldots 4.70947$

$v_{t} = V^{h}_{t} - V_{t} = 5.64425 - 4.70947 \ldots\ldots\ldots\ldots 0.93478$

$w = 0.7167$ g.

$D_{t} = w/v_{t} = 0.7167/0.93478. \ldots\ldots\ldots//\ldots\ldots\ldots 0.7666$

APPENDIX III

SPECIFIC VOLUMES OF MERCURY FROM 0°C to 95°C

The values from 0-40°C are taken from the Chemical Engineers Handbook (Perry), page 358, and those from 40-95°C are calculated from the following equation:

$$V_t = 0.0735540\{1 + 10^{-6}(181.456t + 0.009205t^2 + 0.000006608t^3 + 0.0000000673201t^4)\})$$

Temp.	Spec. Volume	Temp.	Spec. Volume
0.0	0.0735566	25.0	0.0738962
1.0	5694	26.0	9036
2.0	5828	27.0	9170
3.0	5961	28.0	9304
4.0	6095	29.0	9437
5.0	6228	30.0	9571
6.0	6362	31.0	9705
7.0	6496	32.0	9839
8.0	6629	33.0	9973
9.0	6763	34.0	0.0740107
	6893		
10.0	6893	35.0	0241
11.0	7030	36.0	0374
12.0	7164	37.0	0508
13.0	7298	38.0	0642
14.0	7431	39.0	0776
15.0	7565	40.0	0891
16.0	7699	41.0	1024
17.0	7832	42.0	1158
18.0	7966	43.0	1223
19.0	8100	44.0	1426
20.0	8233	45.0	1560
21.0	8367	46.0	1695
22.0	8501	47.0	1829
23.0	8635	48.0	1963
24.0	8768	49.0	2097

APPENDIX III (Continued)

Temp.	Spec. Volume	Temp.	Spec. Volume
50.0	0.0742231	75.0	0.0745587
51.0	2365	76.0	5733
52.0	2500	77.0	5868
53.0	2634	78.0	5996
54.0	2768	79.0	6130
55.0	2903	80.0	6264
56.0	3037	81.0	6399
57.0	3171	82.0	6535
58.0	3305	83.0	6670
59.0	3440	84.0	6804
60.0	3843	85.0	6939
61.0	3709	86.0	7074
62.0	3843	87.0	7209
63.0	3978	88.0	7344
64.0	4112	89.0	7479
65.0	4246	90.0	7584
66.0	4381	91.0	7749
67.0	4516	92.0	7884
68.0	4650	93.0	8019
69.0	4785	94.0	8154
70.0	4919	95.0	8288
71.0	5053		
72.0	5188		
73.0	5322		
74.0	5457		

APPENDIX IV

Hexadecane:

Lower Curve

Temp.	Density.
85.0	0.7264
84.0	0.7282
82.0	0.7294
78.0	0.7324
76.0	0.7336
74.0	0.7354
70.0	0.7383
66.0	0.7412
62.0	0.7440
58.0	0.7464
54.0	0.7496
50.0	0.7524
46.0	0.7552
42.0	0.7579
38.0	0.7608
34.0	0.7637
30.0	0.7666
28.0	0.7681
26.0	0.7695
24.0	0.7709
22.0	0.7729
20.0	0.7736
18.0	0.7748
17.0	0.7761
16.0	0.7760
15.6	0.7765
15.0	0.8471
14.9	0.8536
14.8	0.8613
14.7	0.8707
14.5	0.8774
14.0	0.8937
13.5	0.8981
12.0	0.9046
10.0	0.9080
8.0	0.9099
6.0	0.9109
4.0	0.9120
2.0	0.9129
0.0	0.9137

Upper Curve, same values from 85°C down to 15.6°C.

Temp.	Density.
15.6	0.7765
15.1	0.8398
15.0	0.8465
14.9	0.8501
14.8	0.8526
14.7	0.8543
14.6	0.8556
14.5	0.8571
14.4	0.8584
14.3	0.8596
14.2	0.8607
14.1	0.8615
14.0	0.8625
13.9	0.8632
13.8	0.8640
13.7	0.8651
13.6	0.8655
13.5	0.8661
13.1	0.8686
13.0	0.8691
12.5	0.8712
12.0	0.8743
11.5	0.8749
11.0	0.8759
10.5	0.8774
10.0	0.8781
9.0	0.8795
8.0	0.8810
7.0	0.8823
6.0	0.8836
5.0	0.8854
4.0	0.8864
3.0	0.8876
2.0	0.8890
1.0	0.8902
0.0	0.8916

APPENDIX IV (Continued)

Eicosane:

Liquid Region

Temp.	Density
75.0	0.7573
74.0	0.7581
73.0	0.7583
72.0	0.7587
71.0	0.7600
70.0	0.7601
69.0	0.7603
68.0	0.7609
67.0	0.7616
66.0	0.7620
65.0	0.7628
64.0	0.7635
63.0	0.7640
62.0	0.7631
61.0	0.7651
60.0	0.7656
59.0	0.7661
58.0	0.7666
57.0	0.7675
56.0	0.7676
55.0	0.7686
54.0	0.7689
53.0	0.7695
52.0	0.7699
51.0	0.7705
70.0	0.7712
49.0	0.7711
48.0	0.7718
47.0	0.7726
46.0	0.7733
45.0	0.7735
44.0	0.7741
43.0	0.7749
42.0	0.7755
41.0	0.7748
40.0	0.7763
39.0	0.7771
38.0	0.7776
37.0	0.7782
3630	0.7790

Rising Temperature

Temp.	Density
35.5	0.8978
35.0	0.9065
34.0	0.9108
33.0	0.9108
32.0	0.9102
30.0	0.9102
28.0	0.9106
26.0	0.9124
22.0	0.9149
20.0	0.9159
16.0	0.9180
14.0	0.9190
12.0	0.9199
10.0	0.9207
8.0	0.9214
4.0	0.9229
0.0	0.9242

Falling Temperature

Temp.	Density
36.0	0.8315
35.5	0.8525
34.0	0.8625
33.5	0.8621
33.0	0.8654
32.5	0.8662
32.0	0.8677
31.9	0.8978
31.7	0.9060
31.3	0.9073

APPENDIX IV (Continued)

Docosane:

Liquid Range

Temp.	Density
95.0	0.7462
94.0	0.7466
92.0	0.7505
84.0	0.7531
80.0	0.7556
74.0	0.7596
70.0	0.7620
62.0	0.7672
58.0	0.7696
54.0	0.7721
53.0	0.7733
46.0	0.7785
44.1	0.7797

Temp. Dropping

Temp.	Density
43.5	0.8596
43.0	0.8628
42.0	0.8650
41.0	0.8670
40.0	0.8690
39.8	0.8900
39.6	0.9012
39.4	0.9027
39.0	0.9039

Temp. Rising.

Temp.	Density.
43.4	0.8882
43.0	0.8970
42.8	0.8989
42.4	0.9010
42.0	0.9022
41.0	0.9033
40.0	0.9040
39.0	0.9010
38.0	0.9029
37.0	0.9052
34.0	0.9081
32.0	0.9096
30.0	0.9108
28.0	0.9120
26.0	0.9138
24.0	0.9148
20.0	0.9173
16.0	0.9199
15.0	0.9200
12.0	0.9218
19.0	0.9227
8.0	0.9237
4.0	0.9251
0.0	0.9268

APPENDIX IV (Continued)

Tetracosane:

Temp.	Density.
75.0	0.7621
70.0	0.7651
65.0	0.7681
60.0	0.7713
55.0	0.7744
52.0	0.7764
50.7	0.7772
50.6	0.8468
50.5	0.8601
50.0	0.8616
49.0	0.8648
48.3	0.8658
48.0	0.8663
47.8	0.8722
47.6	0.8932
47.5	0.8939
47.2	0.8974
47.1	0.9136
46.8	0.9147
46.6	0.9172
46.0	0.9205
45.0	0.9306
42.0	0.9322
40.0	0.9347
35.0	0.9340
35.0	0.9354
30.0	0.9370
25.0	0.9386
20.0	0.9399
15.0	0.9397
10.0	0.9409
5.0	0.9420

APPENDIX IV (Continued)

Hexacosane:

Temp.	Density
90.0	0.7565
80.0	0.7642
70.0	0.7707
60.0	0.7768
56.0	0.7793
55.8	0.7796
55.6	0.8574
55.2	0.8607
54.8	0.8623
54.5	0.8634
54.0	0.8640
53.0	0.8658
52.0	0.8672
51.0	0.8688
50.0	0.8702
48.8	0.8722
48.6	0.8960
48.2	0.8992
48.0	0.9020
47.0	0.9055
46.0	0.9060
44.0	0.9071
40.0	0.9097
36.0	0.9120
32.0	0.9145
28.0	0.9169
24.0	0.9193
20.0	0.9219
16.0	0.9241
12.0	0.9266
8.0	0.9290
4.0	0.9313
9.0	0.9340

Hexacosane: (Capillary Heights)

Temperature Rising.
(Checked 4 times)

Temp.	Height
10.9	8.00
12.0	8.28
16.0	9.20
20.0	10.15
24.0	11.10
28.0	12.08
32.0	13.05
36.0	14.02
40.0	15.00
42.0	15.49

Temperature Falling
(Following points make smooth curve with those given above)

Temp.	Height.
44.0	15.95
46.0	16.42
48.0	16.88
49.0	17.10
50.0	17.35
51.0	17.58
51.5	17.70
52.0	17.80
52.2	17.85
52.2	17.89
52.4	17.90
52.6	17.97
52.8	18.05
53.0	18.12
53.1	18.15
53.2	18.20
53.3	18.25
53.4	18.29
53.5	18.34
53.6	18.38
53.7	18.42
53.8	18.49
53.9	18.55
54.0	18.61
54.3	18.75
54.4	18.88
54.6	19.03
54.8	19.21
55.0	19.39

Temp.	Height
55.1	19.50
55.2	19.63
55.3	19.75
55.3	19.90
55.5	20.09
55.6	20.35
55.7	20.90
55.8	25.00
55.9	28.60
56.0	28.60

Temperature Rising

45.0	16.13
46.0	16.18
46.5	16.20
47.0	16.24
47.5	16.28
48.0	16.34
48.2	16.37
48.4	16.39
49.0	16.48
49.5	16.57
50.0	16.70
50.2	16.75
50.4	16.80
50.6	16.85
50.8	16.91
51.0	17.00
51.2	17.06
51.4	17.10
51.6	17.16
51.8	17.124
52.0	17.33
52.2	17.40
52.4	17.49
52.6	17.58
52.8	17.68
53.0	17.78
53.2	17.78
53.4	17.98
53.6	18.00
53.8	18.24
54.0	18.38
54.2	18.54
54.4	18.70
54.6	18.88
54.8	19.08

Hexadosane: (Capillary Heights, continued)

Temperature Rising.

Temp.	Height.
48.2	16.37
48.4	16.39
49.0	16.48
49.5	16.57
50.0	16.70
50.2	16.75
50.4	16.89
50.6	16.85
50.8	16.91
51.0	17.00
51.2	17.06
51.4	17.10
51.6	17.16
51.8	17.24
52.0	17.33
52.2	17.40
52.4	17.49
52.6	17.58
52.8	17.68
53.0	17.78
53.2	17.78
53.4	17.98
53.6	18.10
53.8	18.24
54.0	18.38
54.2	18.54
54.4	18.70
54.6	18.88
54.8	1908
55.0	19.34
55.2	19.56
55.4	19.85
55.6	20.35
56.0	28.60

Readings Down from 95.0°C

Temp.	Height
47.2	14.1 plus
47.3	6.61
48.0	7.12
49.2	7.98
51.0	8.36
52.0	8.90
52.0	9.46
52.5	9.78
53.0	10.17
53.5	10.65
54.0	11.26
54.5	12.00
55.0	13.16

Temperature Falling. Continuous, smooth curve from 95°C.

Temp.	Height
55.2	14.24
55.3	15.19
55.5	18.00
55.8	28.60
57.0	28.88
59.0	29.35
60.0	29.59
62.0	30.08
64.0	30.55
66.0	31.025
68.0	31.61
70.0	32.00
72.0	32.50
74.0	32.99
76.0	33.57
78.0	33.98
80.0	34.47
82.0	34.97
84.0	35.45
86.0	35.94
88.0	36.43
90.0	36.95
92.0	37.55
93.0	37.69
94.0	37.93
95.0	38.22

APPENDIX IV (Continued)

Octacosane:

Temperature	Density
80.0	0.7673
75.0	0.7705
70.0	0.7737
68.0	0.7751
66.0	0.7764
65.8	0.7765
65.7	0.7766
65.6	0.7767
65.4	0.7769
65.3	0.7769
65.2	0.7770
65.0	0.7771
64.5	0.7774
64.0	0.7778
63.2	0.7783
63.0	0.7785
62.5	0.7788
62.0	0.7791
61.4	0.7796
61.2	0.7797
61.2	0.8263
61.0	0.8335
60.5	0.8637
60.0	0.8676
59.5	0.8695
59.0	0.8705
58.5	0.8712
58.0	0.8723
57.5	0.8730
57.0	0.8737
56.5	0.8745
56.0	0.8751
55.5	0.8760
55.0	0.8769
54.0	0.8804
53.0	0.9073
52.0	0.9095
51.0	0.9099
50.0	0.9108
48.8	0.9117
45.0	0.9131
40.0	0.9159
34.9	0.9182
30.0	0.9204
25.0	0.9228
17.3	0.9263
8.0	0.9297
0.0	0.9324

APPENDIX IV (Continued)

Nonacosane:

Temperature	Density
80.0	0.7696
75.0	0.7727
70.0	0.7760
68.0	0.7774
66.0	0.7785
65.8	0.7787
65.7	0.7788
65.6	0.7789
65.5	0.7790
65.4	0.7792
65.3	0.7793
65.2	0.7793
65.0	0.7795
66.5	0.7798
64.0	0.7800
63.2	0.7807
63.0	0.7825
63.0	0.7832
62.5	0.7936
62.0	0.7939
61.4	0.7952
61.2	0.7953
61.0	0.7953
60.5	0.7960
60.0	0.7968
59.5	0.7970
59.0	0.7970
58.5	0.7968
58.0	0.7983
57.5	0.7990
57.0	0.8088
56.5	0.8139
56.0	0.8143
55.5	0.8142
55.0	0.8142
54.0	0.8150
53.0	0.8179
52.0	0.8191
51.0	0.8199
50.0	0.8207
48.0	0.8224
45.0	0.8249
40.0	0.8282
34.9	0.8320
30.0	0.8371
25.0	0.7404
17.3	0.8450
8.0	0.8494
0.0	0.8523

APPENDIX IV (Continued)

Triacontane:

Temp.	Density	Temp.	Density.
80.0	0.7731	59.5	0.9172
75.0	0.7763	59.0	0.9214
70.0	0.7795	58.5	0.9236
68.0	0.7808	58.0	0.9238
66.0	0.7819	57.5	0.9242
65.8	0.7821	57.0	0.9246
65.7	0.7822	56.5	0.9243
65.6	0.7822	56.0	0.9253
65.5	0.7823	55.5	0.9256
65.3	0.7824	55.0	0.9259
65.3	0.8098	54.0	0.9270
65.3	0.8160	53.0	0.9275
65.2	0.8612	52.0	0.9280
65.0	0.8689	51.0	0.9285
64.5	0.8720	50.0	0.9291
64.0	0.8731	48.0	0.9305
63.2	0.8743	45.0	0.9321
63.0	0.8746	40.0	0.9350
62.5	0.8753	34.9	0.9372
62.0	0.8761	30.0	0.9396
61.4	0.8771	25.0	0.9423
61.2	0.8774	17.3	0.9453
61.0	0.8777	8.0	0.9488
60.5	0.8784	0.0	0.9512
60.0	0.8801		

APPENDIX IV (Continued)

Dotriacontane:

Temp.	Density.
86.75	0.7715
80.08	0.7756
75.0	0.7787
73.0	0.7801
71.0	0.7816
69.1	0.7827
68.1	0.8628
67.0	0.8708
66.0	0.8738
65.0	0.8758
63.95	0.8780
63.5	0.8780
63.0	0.8885
62.5	0.9080
62.4	0.9102
62.24	0.9113
62.0	0.9122
60.0	0.9156
55.0	0.9208
47.6	0.9271
47.3 [redacted]	0.9329
42.8	0.9300
49.95	0.9252
45.12	0.9286
40.12	0.9310
35.03	0.9345
30.6	0.9366
24.7	0.9293
21.2	0.9399
15.4	0.9450
9.25	0.9445
0.10	0.9471

APPENDIX IV (Continued)

Tetratriacontane:

Temperature.	Density.
95.0	0.7716
90.0	0.7751
85.0	0.7781
80.0	0.7810
74.0	0.7847
72.9	0.7853
72.4	0.8550
72.2	0.8650
72.0	0.8686
71.8	0.8716
71.6	0.8734
71.4	0.8748
71.2	0.8760
71.0	0.8770
70.5	0.8788
70.0	0.8798
69.0	0.8820
68.2	0.8836
68.0	0.9040
67.5	0.9136
67.0	0.9170
66.5	0.9192
66.0	0.9206
64.0	0.9232
62.0	0.9249
60.0	0.9260
55.0	0.9292
50.0	0.9320
45.0	0.9348
40.0	0.9370
35.0	0.9397
30.0	0.9422
25.0	0.9443
20.0	0.9468
15.0	0.9486
10.0	0.9502
5.0	0.9519
0.0	0.9520